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Biosorption of Copper, Nickel and Manganese Using Non-Living Biomass of Marine Alga, *Ulva lactuca*

Hanan Hafez Omar

Department of Botany, Faculty of Science, Tanta University, Tanta, Egypt

Abstract: The adsorption of Cu^{2+} , Ni^{2+} and Mn^{2+} onto the marine algal biomass of *Ulva lactuca* was investigated in single and multimetal solutions. This study was intended to determine the role of different pH values (2-8) on the biosorption of metals at different concentrations (10, 20 and 30 mg L⁻¹). The biosorption capacity of Cu^{2+} , Ni^{2+} and Mn^{2+} for 10 mg L⁻¹ was the same as 20 and 30 mg L⁻¹, increase with increasing pH up to pH 5.0 and then decreased, in single and multimetal solutions. The optimum pH value was observed in the pH range 4-5 for Cu^{2+} and pH 5-6 for Ni^{2+} and Mn^{2+} . The maximum biosorption capacities of tested alga for Cu^{2+} , Ni^{2+} and Mn^{2+} were 92, 80 and 75%, respectively in single metal solution at 10 mg L⁻¹ and pH 5.0. At a further increase of pH (8.0) the biosorption process for Cu^{2+} , Ni^{2+} and Mn^{2+} (75, 69 and 63%, respectively at 10 mg L⁻¹) was decreased. The minimum biosorptions were 60, 49 and 44% for Cu^{2+} , Ni^{2+} and Mn^{2+} , respectively in single metal solution at 10 mg L⁻¹ and pH 2.0. In the multimetal solution, algal biomass exhibited the maximum and the minimum biosorption capacity at different pH values the same as in single metal solution. The inhibitory role of other ions on sorption process can be well observed in multimetal mixture, where biosorption capacity of Cu^{2+} , Ni^{2+} and Mn^{2+} were significantly decreased in the multimetal solutions. The maximum biosorption was recorded for Cu^{2+} (83%) in solution of $\text{Cu}^{2+} + \text{Mn}^{2+}$, Mn^{2+} (67%) in solution of $\text{Ni}^{2+} + \text{Mn}^{2+}$ and for Ni^{2+} (74%) in solution of $\text{Ni}^{2+} + \text{Mn}^{2+}$ at the concentration 10 mg L⁻¹ and pH 5.0. The observed reduction in the biosorption of Cu^{2+} , Ni^{2+} and Mn^{2+} (65, 57 and 52%, respectively at 10 mg L⁻¹ and pH 5.0) was more pronounced in the multimetal solution of $\text{Cu}^{2+} + \text{Ni}^{2+} + \text{Mn}^{2+}$ as compared with single metal solution. The results demonstrated that the affinity of the tested alga for sorption of the investigated metal ions in single and multimetal solutions runs in the order $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$. Biosorption equilibrium was established by the Langmuir and Freundlich isotherm models. According to the analyses conducted, the biosorption of Cu^{2+} , Ni^{2+} and Mn^{2+} to *Ulva lactuca* was more consistent with Freundlich isotherm.

Key words: pH, heavy metals, biosorption, adsorption isotherm, *Ulva lactuca*

INTRODUCTION

Heavy metals are major pollutants in marine, lake and ground waters as well as in industrial and even treated effluents and they can create serious environmental pollution and threatened biolife (Bishop, 2002; Francois *et al.*, 2007; Pistocchi *et al.*, 2000; Tekerlekopoulou *et al.*, 2007; Vijayaraghavan *et al.*, 2005; Yu *et al.*, 1999). Heavy metals can be extremely toxic as they damage nerves, liver, kidney and bones and also block functional groups of vital enzymes affecting the biochemical and physiological processes (Kumar and Kaladharan, 2006; Travieso *et al.*, 1999). For more than a decade, researchers have been looking for cheaper and more effective methods to remediate heavy metal-contaminated water and reduce the growing public-health risk (Farah and Sneddon, 1992; Wilde and Benemann, 1993). The major advantages of biosorption over conventional treatment methods include low cost, high efficiency of metal removal from dilute solution,

minimization of chemical and/or biological sludge, no additional nutrient requirement, regeneration or biosorbent and the possibility of metal recovery (Kratochvil and Volesky, 1998; Omar, 2002; Radway *et al.*, 2001). Sorption capacities are generally similar between live and dead biomass of a specific type (Sandau *et al.*, 1996). Many studies have shown that the factors influencing biosorption by non-viable algae include pH (Hassett *et al.*, 1981; Yu and Kaewsarn, 1999), heavy metal species (Fourest and Volesky, 1997), competing ions (Lau *et al.*, 1999) and the type of algae (Radway *et al.*, 2001). Tuzun *et al.* (2005) recorded that the biomacromolecules on the algal cell surface have several functional groups (such as, amino, carboxyl, thiol, sulfhydryl and phosphate groups). The metal biosorption depends on the protonation or unprotonation of these functional groups on the surface of the cell wall. The ionic forms of the metal ions in solution and the electrical charge of the algal cell wall components (i.e., functional groups carrying polysaccharides and proteins) depend on

the solution pH. On the other hand, too high pH value can cause precipitation of metal complexes. For different biosorption system of metal ions, the optimal pH is different. Usually industrial effluents contain a number of metal compounds which will interfere with the sorption potential of the sorbent. Therefore, a multimetal sorption was selected for the study, as it would more closely represent the composition of industrial effluents. Marine macro algae are harvested or cultivated in many part of the world and are therefore readily available in large quantities for the development of highly effective biosorbent materials. This study investigated the biosorption potential of the marine macro-algae *Ulva lactuca* on Cu^{2+} , Ni^{2+} and Mn^{2+} in single and multimetal aqueous solutions and the pH required for sorption. The uptake capacities of algal biomass for metal ions in aqueous solutions were evaluated from Langmuir and Freundlich equilibrium isotherms.

MATERIALS AND METHODS

Preparation of algal biomass (biosorbents): Fresh sample of green alga (*Ulva lactuca*) were harvested in March from Abu-Qir beach on the coast of Mediterranean Sea at Alexandria, Egypt. The biomass of algae was rinsed with tap water and extensively washed with distilled water in Laboratory. It was dried in sunlight and then dried in an oven at 50°C overnight. Dried biomass was ground in a blender and sorted by sieving using the standard sieve (size of particles = 0.8-1.0 mm).

Preparation of heavy metals solutions for biosorption: The sulphate salts $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were dissolved in distilled deionized water in single (Cu^{2+} , Ni^{2+} and Mn^{2+}) and multimetal ($\text{Cu}^{2+} + \text{Ni}^{2+}$, $\text{Cu}^{2+} + \text{Mn}^{2+}$, $\text{Ni}^{2+} + \text{Mn}^{2+}$ and $\text{Cu}^{2+} + \text{Ni}^{2+} + \text{Mn}^{2+}$) systems at different concentrations 10, 20 and 30 mg L⁻¹ each.

Effect of pH: The effect of pH on the biosorption capacity of single and multimetal solutions at the different concentrations (10, 20 and 30 mg L⁻¹) was investigated in the algal culture at the pH range of 2-8. The pH of each solution was adjusted to the required value with diluted or concentrated HCl and NaOH solutions before being mixed with algal solution using ORION Research model 201/digital pH meter.

Biosorption experiments: The biosorption experiments were conducted in 125 mL Erlenmayer flasks. 0.2 g dry weight of *Ulva lactuca* was conducted with the different concentrations of aqueous metal solutions at the different pH values (2-8). The flasks placed on a shaker (Julabo SW-20C) with constant shaking at 100 rpm for one hour. After the exposure time, the mixture was centrifuged and

the supernatant decanted and determined for metal content. Final metal concentrations in solutions were determined using Perkin-Elmer Atomic Absorption Spectrophotometer Model 2380. The obtained data were presented in the form of percentage biosorption (%) using the following formula according to Marungrueng and Pavasant (2006):

$$\text{Biosorption \%} = [(C_0 - C_e) / C_0] \times 100$$

where, C_0 is the initial metal concentration in the aqueous phase expressed as mg L⁻¹ and C_e is the final metal concentration in the aqueous phase expressed as mg L⁻¹.

Data evaluation: Sorption models were:

a). The Langmuir model, $C/Y = C(1/Y_m) + 1/(KY_m)$

where, Y_m is the maximum amount of metal adsorbed (mg g⁻¹), the slope = $1/Y_m$, K is the equilibrium constant related to the affinity of binding site, C is the residual metal concentration (mg), Y is the adsorption at residual metal concentration (mg g⁻¹). The essential characteristics of the Langmuir isotherm can be expressed in terms of equilibrium parameter R which is defined by the following equation: $R = 1 / [1 + (K C_0)]$ (Nassar *et al.*, 1995) where C_0 is the equilibrium concentration.

Value of R	Type of isotherm
$R > 1$	Unfavourable
$R = 1$	Linear
$0 < R < 1$	Favourable
$R = 0$	Irreversible

b). The Freundlich model, $\log(x/m) = \log K + 1/n(\log C)$. Where x is the amount of adsorbate, m is the amount of adsorbing material, C is the equilibrium concentration of adsorbate in the solution, K and n are Freundlich constant and are the indicators of the adsorption capacity and adsorption intensity, respectively.

Statistics: Results were tested by one-way analysis of variance (ANOVA). ANOVA effects and treatments differences were considered significant at $p < 0.05$.

RESULTS AND DISCUSSION

Effect of pH: Since pH is one of the main variables affecting the biosorption process, the optimum pH value for the uptake of single and multimetal solutions were determined. ANOVA showed that the differences in the biosorption capacity for tested heavy metals at different pH values were statistically significant. Figure 1 showed the biosorption capacity of *Ulva lactuca* for Cu^{2+} , Ni^{2+} and

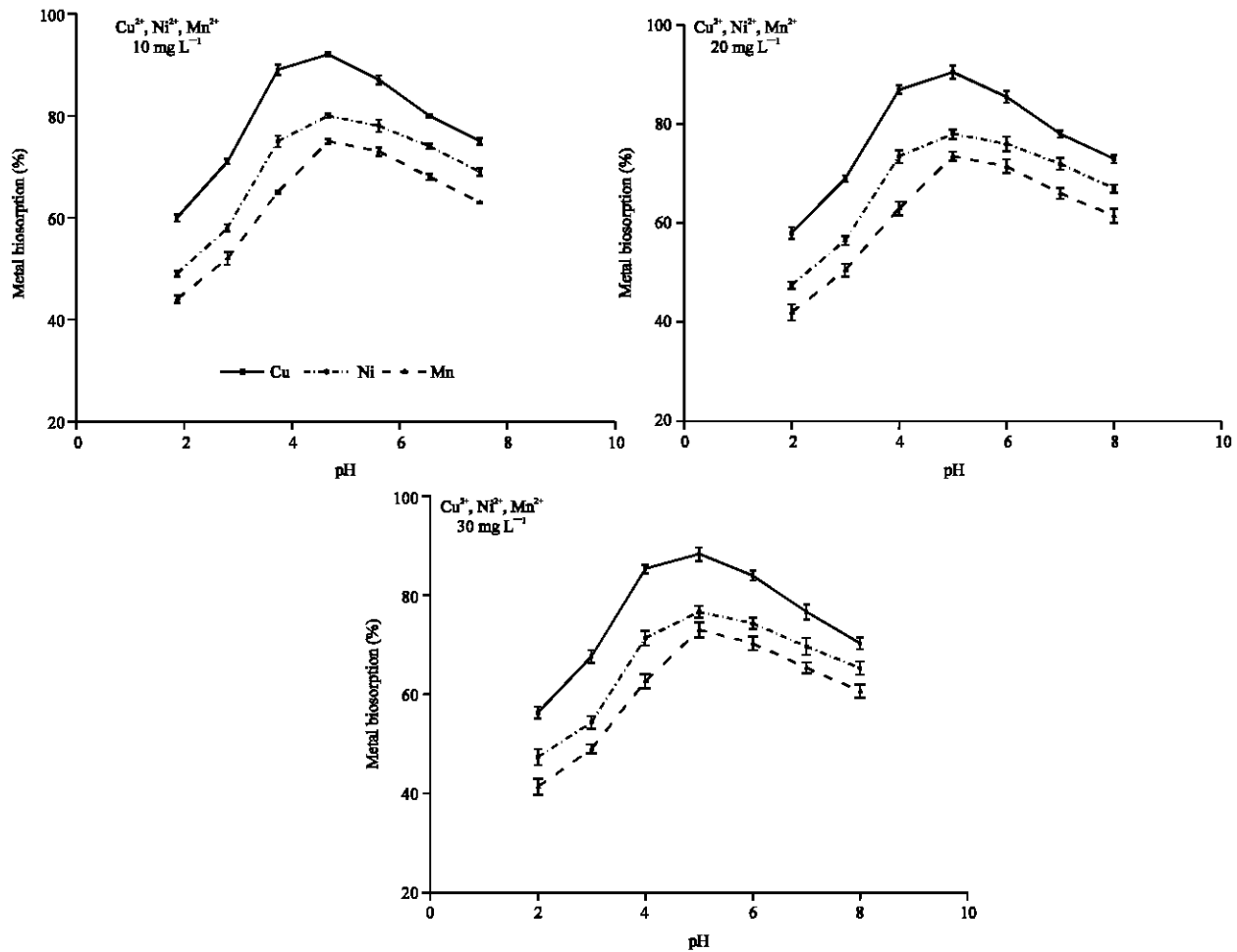


Fig. 1: Effect of pH values on the biosorption of Cu^{2+} , Ni^{2+} and Mn^{2+} ions at the concentrations 10, 20 and 30 mg L^{-1} each in single metal solution by biomass of *Ulva lactuca* (n = 3)

Mn^{2+} in single metal solutions at the different concentrations 10, 20 and 30 mg L^{-1} . The results revealed that the percentage of the biosorption capacity for 20 and 30 mg L^{-1} metals the same as 10 mg L^{-1} , increase with increasing pH value up to pH 5.0 and then decreased (Table 1). The maximum biosorption capacity of 10, 20 and 30 mg L^{-1} Cu^{2+} (92, 90 and 88%, respectively), Ni^{2+} (80, 78 and 76%, respectively) and Mn^{2+} (75, 73 and 71%, respectively) was observed at pH 5.0. The affinity order was $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$. The increase in biosorption levels with an increase in pH can be explained by the influence of the number of negative surface charges, which depends on the dissociation of functional groups (Feng and Aldrich, 2004). The pH depends of metal uptake can largely be related to the functional groups present in algae and also on the metal chemistry in solution (Matheickal *et al.*, 1999). Davis *et al.* (2003) found that majority of metals display maximal or near maximal sequestration at pH value near the apparent dissociation

constant of carboxylic acid observed in algal biomass (pH near 5). Wang and Chen (2006) reported that the divalent positive ions are suitable to interact with negatively charged groups in biomass at pH 5.0. On the other hand, the outer layer of the cell wall contains protein which can cause a change through dissociation of the ionisable side groups of the amino acids. The ionic state of ligands such as carboxyl, phosphate and amino groups will promote reaction with the positively charged metal ion.

The binding of Cu^{2+} , Ni^{2+} and Mn^{2+} in single metal solution was reduced below pH 4.0. In Fig. 1 the biosorption capacity of 10 mg L^{-1} for Cu^{2+} , Ni^{2+} and Mn^{2+} (89, 75 and 65%, respectively) at pH 4.0 was higher than that at pH 3.0 (71, 58, 52%, respectively). Ricou *et al.* (1999) found that the electrostatic attraction to negatively charged functional groups may be one of the specific biosorption mechanisms at pH 4.0. At pH 4.0 the most important group is phosphate and the other two main active molecular groups are carboxyl and sulphate.

Therefore, the difference in the sorbent loadings was mainly attributed to the difference in the adsorption of the heavy metals on the sorbents at varied pH. At the same time, Igwe *et al.* (2005) showed that the binding of metals was very low below pH 4.0. This is a result of the ion exchange between metal ions and H⁺. Since both metal ions and H⁺ compete for the same binding sites, higher concentrations of each ion can displace the other ion from the binding sites as proposed by several authors (Fourest and Roux, 1992; Huang *et al.*, 1991; Mentler *et al.*, 2005; Schiewer, 1999).

From these data it was clear that the maximum reduction in single metal biosorption for Cu²⁺, Ni²⁺ and Mn²⁺ at the concentration was observed at pH 2.0 (60, 49 and 44%, respectively) (Fig. 1). At a low pH, of almost 2.0, the interaction of heavy metal ions with algal biomass could be primarily with the carboxylate groups of the cell wall components of the algae (Aldor *et al.*, 1995; Gupta *et al.*, 2000). Hence, at low pH, i.e., high proton concentrations, the binding of protons will increase and

lead to reduced Cu²⁺, Ni²⁺ and Mn²⁺ binding for any given concentration of metals.

However, at higher pH values (7-8) the metal biosorption decreased in single metal solutions at the different concentrations (Fig. 1). At pH 8.0, Cu²⁺, Ni²⁺ and Mn²⁺ biosorption were 75, 69 and 63%, respectively at the metal concentration 10 mg L⁻¹. Tuzun *et al.* (2005) reported that hydrolysis of metal ions becomes significant between pH 7.5 and 8.5. Hawari and Mulligan (2006) and Kamel *et al.* (2004) obtained a similar conclusion. They found that at a further increase of pH (6-9) the solubility of metal decreases enough for precipitation of the metal hydroxide to occur. At acidic pH metals exist in free ionic forms, whereas at alkaline pH they tend to precipitate as insoluble carbonate, phosphates, sulphides, oxides or hydroxide (Rai *et al.*, 1981).

The Fig. 2-5 clarified that the all tested metal ions biosorption was maximum at pH 5.0 the same as in single metal solution. The inhibitory rule of the other ions on sorption process in multimetal solution can be well

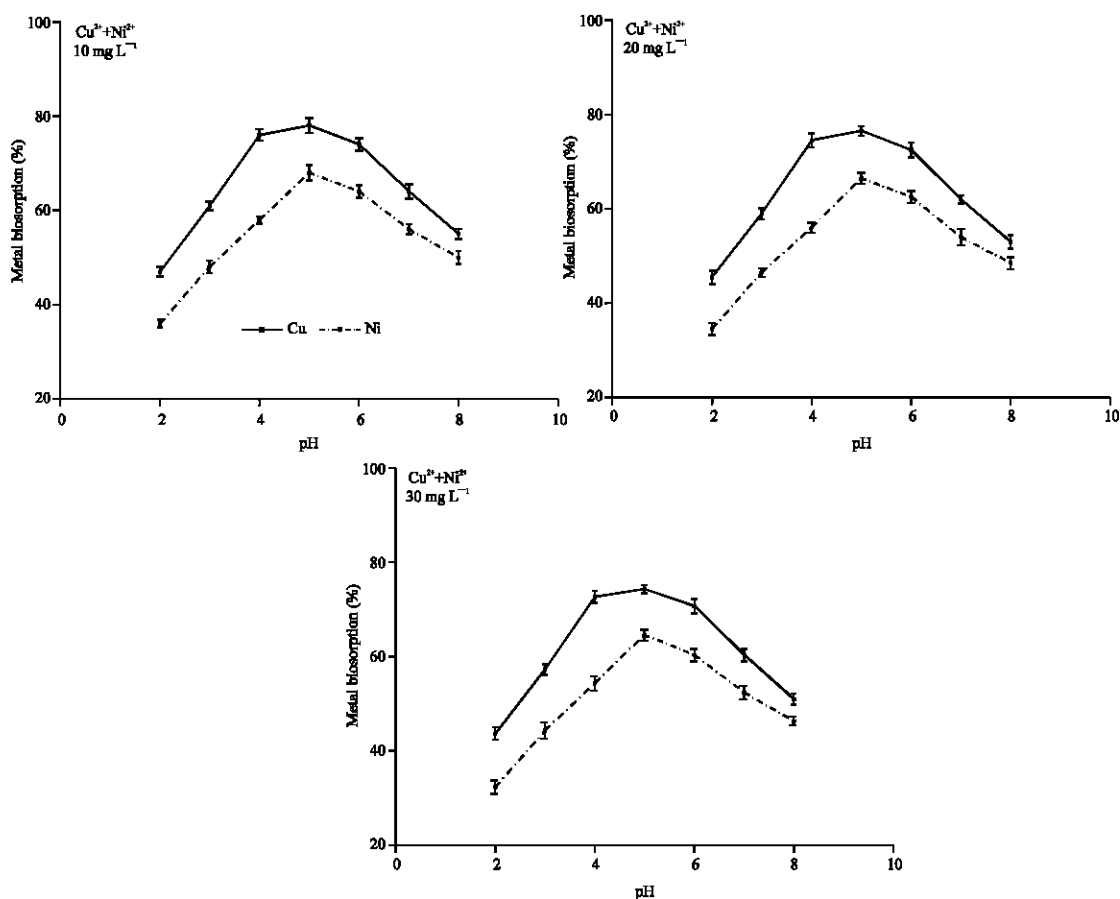


Fig. 2: Effect of pH values on the biosorption of Cu²⁺ and Ni²⁺ ions at the concentrations 10, 20 and 30 mg L⁻¹ each in multimetal solution by biomass of *Ulva lactuca* (n = 3)

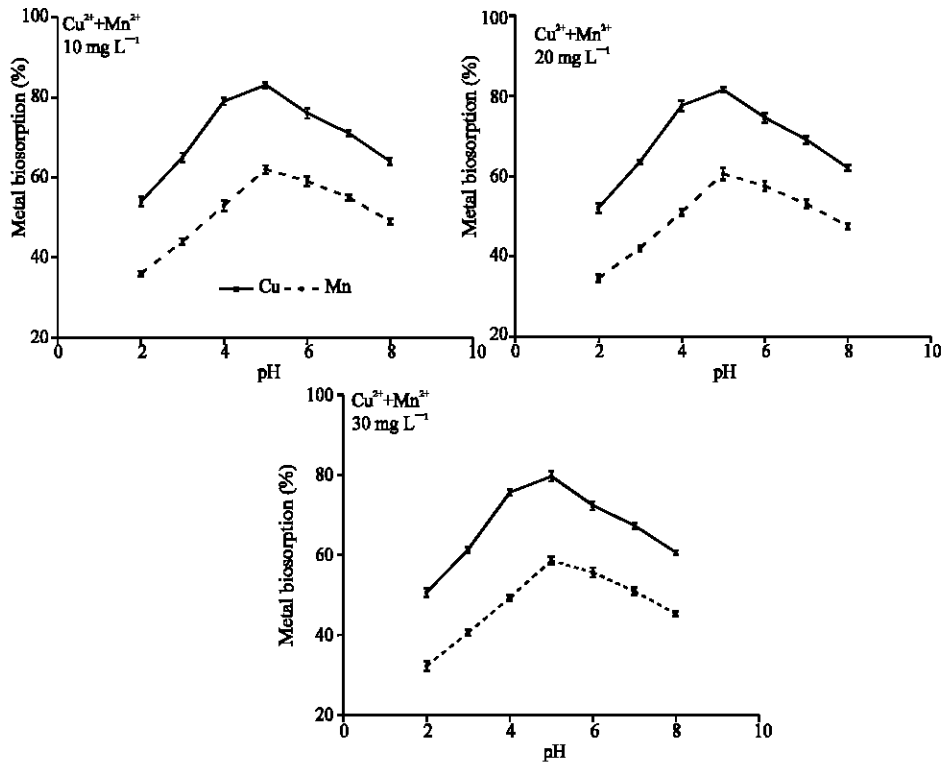


Fig. 3: Effect of pH values on the biosorption of Cu^{2+} and Mn^{2+} ions at the concentrations 10, 20 and 30 mg L^{-1} each in multimetal solution by biomass of *Ulva lactuca* (n = 3)

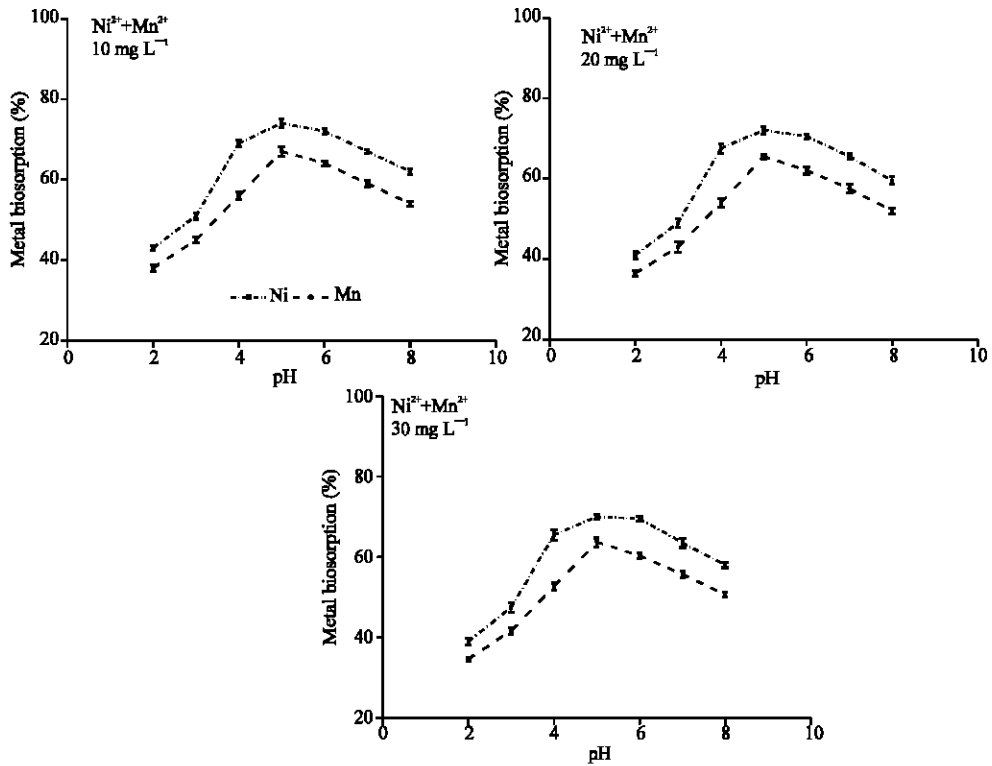


Fig. 4: Effect of pH values on the biosorption of Ni^{2+} and Mn^{2+} ions at the concentrations 10, 20 and 30 mg L^{-1} each in multimetal solution by biomass of *Ulva lactuca* (n = 3)

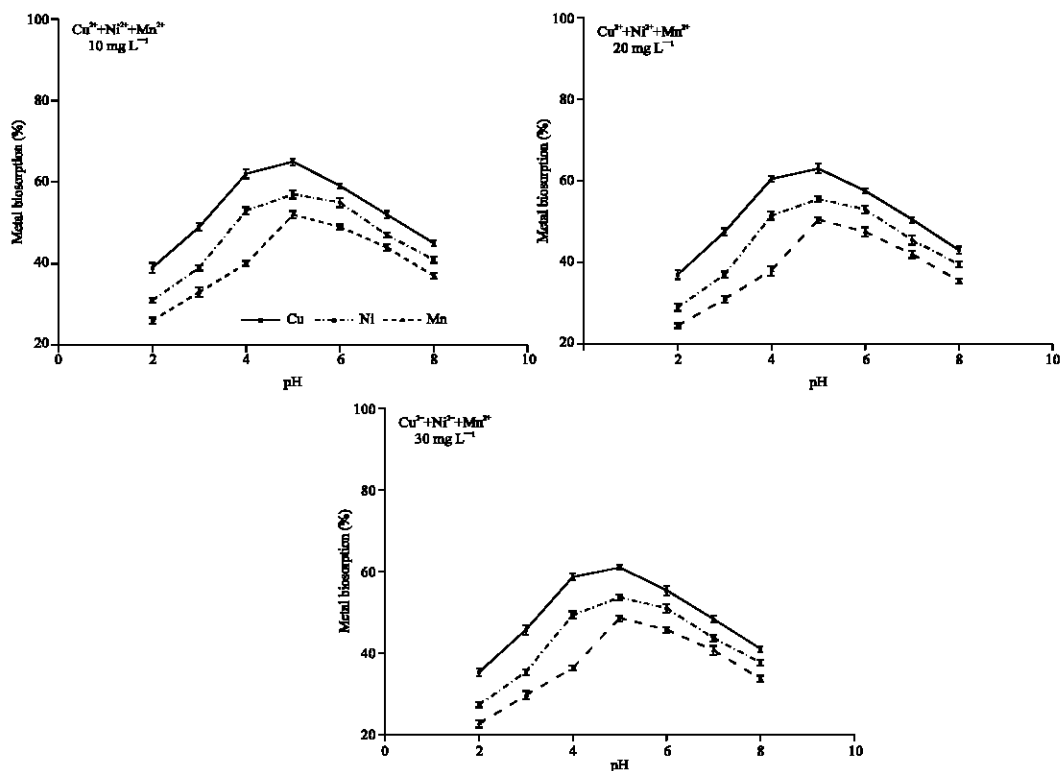


Fig. 5: Effect of pH values on the biosorption of Cu^{2+} , Ni^{2+} and Mn^{2+} ions at the concentrations 10, 20 and 30 mg L^{-1} each in multimetal solution by biomass of *Ulva lactuca* (n = 3)

understood by comparing the metal biosorption capacities of the biosorbent in the case of single at 10 mg L^{-1} metal concentration. As shown in the results, the biosorption of Cu^{2+} at 10 mg L^{-1} (92%) in single metal solution (Fig. 1) was more efficient than that in the multimetal solutions of $\text{Cu}^{2+} + \text{Ni}^{2+}$ (78%, Fig. 2), $\text{Cu}^{2+} + \text{Mn}^{2+}$ (83%, Fig. 3) and $\text{Cu}^{2+} + \text{Ni}^{2+} + \text{Mn}^{2+}$ (56%, Fig. 5). However, Ni^{2+} binding capacity in the multimetal solutions $\text{Cu}^{2+} + \text{Ni}^{2+}$ (68%, Fig. 2), $\text{Ni}^{2+} + \text{Mn}^{2+}$ (74%, Fig. 4) and $\text{Cu}^{2+} + \text{Ni}^{2+} + \text{Mn}^{2+}$ (57%, Fig. 5) showed reduction as compared with single Ni^{2+} solution (80%, Fig. 1). On the other hand, the reduction in Mn^{2+} biosorption was observed in the multimetal solutions of $\text{Cu}^{2+} + \text{Mn}^{2+}$ (62%, Fig. 3), $\text{Ni}^{2+} + \text{Mn}^{2+}$ (67%, Fig. 4) and $\text{Cu}^{2+} + \text{Ni}^{2+} + \text{Mn}^{2+}$ (52%, Fig. 5) as compared with Mn^{2+} biosorption in single solution (75%, Fig. 1). As shown from the results, the maximum reduction in the biosorption process of different metals was observed in the multimetal solution of $\text{Cu}^{2+} + \text{Ni}^{2+} + \text{Mn}^{2+}$ indicating the existence of competitive binding with algal cell surface. The order of the biosorption capacities in the multimetal solutions was $\text{Cu}^{2+} > \text{Ni}^{2+} > \text{Mn}^{2+}$ the same as in the single metal solutions. The higher biosorption of Cu^{2+} might be attributed to the physical aspects of the adsorption process (Tuzun *et al.*, 2005). The ionic radius of Cu^{2+} , 1.28' is larger than that of Ni^{2+} (1.24') and thus a stronger physical affinity for Cu^{2+} is expected at the adsorption

sites on the cells (Weast *et al.*, 1988). The reason why the Cu^{2+} biosorption capacity is higher than the other metal ions is that the flow rate for Cu^{2+} occurred earlier than that for others (Vengris *et al.*, 2001). In the initial stage of sorption, the solutes compete for available sites and metals with stronger binding affinities (i.e., Cu^{2+}) competed more effectively with preferential removal from solution. The algal biomass exhibited the highest biosorption for metal ions in solution of single metal, indicating that complex inter actions of several factors such as ionic charge, ionic radii and electrode potential affect the biosorption of metal ions on the algal biomass. It can be concluded that the algal surface contains a variety of functional groups, these groups that serve as adsorption sites may differ both with respect to the strength of the metal sportive bond and the rate of adsorption onto the sites (Kratochvil *et al.*, 1997). Many of the functional groups present on the algal cell wall and different cations compete for the same binding sites (Fortin *et al.*, 2007; Kola and Wilkinson, 2005; Yan and Viraraghavan, 2003).

Adsorption isotherm: The adsorption isotherm models were used to characterize the interaction of Cu^{2+} , Ni^{2+} and Mn^{2+} with the algal biomass. As shown in Table 1 and 2, the values of K_f and n were higher than that of K. The

Table 1: The Langmuir constants and correlation coefficient of isotherm model for the biosorption of Cu²⁺, Ni²⁺ and Mn²⁺ in single and multimetal aqueous solutions at different pH values by *Ulva lactuca*

Langmuir constants												
pH	Y _m			K			R			R ²		
	Cu	Ni	Mn	Cu	Ni	Mn	Cu	Ni	Mn	Cu	Ni	Mn
Cu, Ni, Mn												
8	72.34	89.75	132.7	0.046	0.027	0.013	0.684	0.788	0.881	0.996	0.993	0.949
7	92.00	77.33	120.0	0.048	0.041	0.019	0.677	0.711	0.842	0.968	0.999	0.855
6	85.26	86.97	119.4	0.087	0.045	0.024	0.534	0.691	0.806	0.997	0.990	0.987
5	59.84	92.00	153.3	0.227	0.048	0.021	0.306	0.677	0.829	1.000	0.968	0.852
4	68.35	89.00	134.4	0.136	0.037	0.015	0.424	0.731	0.873	0.983	0.990	0.726
3	98.01	81.65	89.2	0.027	0.018	0.013	0.788	0.846	0.886	0.972	0.990	1.000
2	83.89	148.90	81.8	0.019	0.007	0.010	0.839	0.937	0.908	0.994	0.661	0.859
Cu + Ni												
8	71.53	70.13	-	0.019	0.015	-	0.844	0.867	-	0.980	0.980	-
7	87.41	79.13	-	0.022	0.017	-	0.820	0.852	-	0.995	0.995	-
6	97.27	87.41	-	0.032	0.022	-	0.759	0.820	-	0.985	0.985	-
5	86.97	97.62	-	0.045	0.023	-	0.691	0.810	-	0.997	0.997	-
4	96.09	81.65	-	0.036	0.018	-	0.736	0.846	-	0.995	0.995	-
3	84.89	66.74	-	0.020	0.015	-	0.834	0.870	-	0.980	0.980	-
2	71.42	44.13	-	0.013	0.014	-	0.883	0.878	-	0.975	0.975	-
Cu + Mn												
8	95.51	-	68.46	0.020	-	0.015	0.834	-	0.869	0.980	-	0.980
7	89.96	-	71.53	0.030	-	0.019	0.772	-	0.844	0.995	-	1.000
6	88.46	-	90.65	0.039	-	0.017	0.719	-	0.855	0.985	-	0.995
5	87.28	-	93.84	0.062	-	0.019	0.618	-	0.843	0.997	-	0.996
4	93.25	-	74.87	0.044	-	0.016	0.694	-	0.861	0.995	-	0.995
3	88.07	-	65.49	0.023	-	0.013	0.815	-	0.886	0.980	-	0.979
2	83.72	-	44.13	0.015	-	0.014	0.870	-	0.878	0.975	-	0.975
Ni + Mn												
8	-	79.11	83.72	-	0.022	0.015	-	0.817	0.870	-	0.962	0.976
7	-	92.99	90.65	-	0.024	0.017	-	0.810	0.855	-	0.992	0.995
6	-	127.10	87.41	-	0.021	0.022	-	0.823	0.820	-	0.972	0.994
5	-	82.88	97.26	-	0.038	0.022	-	0.726	0.817	-	0.999	0.997
4	-	93.62	86.71	-	0.026	0.016	-	0.796	0.864	-	0.993	0.976
3	-	75.10	67.50	-	0.015	0.013	-	0.871	0.885	-	0.989	0.979
2	-	52.83	52.96	-	0.016	0.012	-	0.865	0.889	-	1.000	0.991
Cu + Ni + Mn												
8	56.27	59.30	50.82	0.016	0.013	0.012	0.864	0.888	0.889	0.996	0.992	0.991
7	73.34	71.42	65.49	0.016	0.013	0.013	0.863	0.883	0.886	0.968	0.993	0.979
6	82.80	71.53	75.19	0.019	0.019	0.014	0.842	0.844	0.880	0.997	1.000	0.994
5	81.28	88.10	80.48	0.025	0.016	0.014	0.801	0.861	0.874	1.000	0.995	0.994
4	93.84	74.87	51.92	0.019	0.016	0.014	0.843	0.861	0.878	0.983	0.981	0.997
3	75.19	49.98	42.29	0.014	0.014	0.013	0.880	0.878	0.888	0.972	0.997	0.983
2	49.98	34.43	27.93	0.014	0.014	0.014	0.878	0.875	0.878	0.994	0.998	0.987

Table 2: The Freundlich constants and correlation coefficient of isotherm model for the biosorption of Cu²⁺, Ni²⁺ and Mn²⁺ in single and multimetal aqueous solutions at different pH values by *Ulva lactuca*

Freundlich constants										
pH	K _f			n			R ²			
	Cu	Ni	Mn	Cu	Ni	Mn	Cu	Ni	Mn	
Cu, Ni, Mn										
8	17.78	13.00	9.52	1.23	1.16	1.09	0.996	1.000	1.000	
7	22.30	16.76	11.96	1.19	1.21	1.11	1.000	0.998	1.000	
6	35.13	20.13	15.08	1.23	1.19	1.12	0.999	1.000	1.000	
5	53.98	22.30	16.27	1.40	1.19	1.10	0.993	1.000	1.000	
4	41.38	17.23	10.35	1.31	1.18	1.10	1.000	0.997	0.999	
3	14.06	8.27	6.37	1.15	1.14	1.12	1.000	0.998	0.999	
2	8.94	5.29	4.63	1.15	1.06	1.11	1.000	0.999	1.000	
Cu + Ni										
8	7.50	6.12	-	1.16	1.14	-	0.999	0.998	-	
7	10.51	7.66	-	1.15	1.14	-	1.000	1.000	-	
6	16.22	10.51	-	1.16	1.15	-	0.998	0.998	-	
5	20.13	12.28	-	1.19	1.14	-	0.997	0.999	-	
4	17.93	8.27	-	1.17	1.14	-	0.998	1.000	-	
3	9.31	5.69	-	1.15	1.14	-	1.000	0.998	-	
2	5.38	3.66	-	1.13	1.16	-	0.999	0.997	-	

Table 2: Continued

Freundlich constants									
pH	K _f			n			R ²		
	Cu	Ni	Mn	Cu	Ni	Mn	Cu	Ni	Mn
Cu + Mn									
8	10.36	-	5.90	1.14	-	1.14	1.000	-	0.973
7	14.23	-	7.50	1.16	-	1.16	1.000	-	0.999
6	18.13	-	8.47	1.18	-	1.13	0.997	-	0.999
5	26.75	-	9.55	1.21	-	1.13	0.998	-	0.999
4	21.07	-	6.84	1.18	-	1.14	0.998	-	1.000
3	10.95	-	4.82	1.15	-	1.13	0.998	-	1.000
2	6.99	-	3.66	1.13	-	1.16	1.000	-	0.997
Ni + Mn									
8	-	9.82	6.99	-	1.16	1.13	-	0.982	1.000
7	-	11.84	8.47	-	1.15	1.13	-	0.992	0.999
6	-	14.28	10.51	-	1.11	1.15	-	0.972	1.000
5	-	16.58	11.76	-	1.19	1.14	-	0.999	0.999
4	-	12.92	7.54	-	1.15	1.13	-	0.993	1.000
3	-	6.30	5.00	-	1.14	1.13	-	0.989	1.000
2	-	4.83	3.85	-	1.17	1.14	-	1.000	0.998
Cu + Ni + Mn									
8	5.19	4.31	3.71	1.16	1.14	1.15	0.999	0.999	0.998
7	6.59	5.38	4.82	1.14	1.13	1.13	0.998	0.999	1.000
6	8.60	7.50	5.79	1.14	1.16	1.13	0.998	0.999	0.999
5	11.10	7.84	6.48	1.17	1.13	1.13	0.999	0.999	0.999
4	9.55	6.84	4.24	1.13	1.14	1.16	0.999	0.998	1.000
3	5.79	4.09	3.18	1.13	1.16	1.16	0.999	1.000	1.000
2	4.09	3.03	2.41	1.16	1.18	1.19	1.000	0.999	0.997

higher the values of K_f and n the lower the value of K, the higher the affinity of algae (Jalali *et al.*, 2002). The results also show that the values of K, K_f and n for Cu²⁺ were higher than those for Ni²⁺ and Mn²⁺. From these observations, algal biomass could have a high adsorption capacity and high binding affinity for Cu²⁺ compared to Ni²⁺ and Mn²⁺. Therefore, the general affinity sequence is Cu²⁺ > Ni²⁺ > Mn²⁺. The values of the Freundlich exponent, n, are greater than one, indicating that Cu²⁺, Ni²⁺ and Mn²⁺ are favorably adsorbed by *U. lactuca*. The correlation coefficient (R²) for biosorbent shows the most suitable model for describing these sorption processes. The biosorption of Cu²⁺, Ni²⁺ and Mn²⁺ to *U. lactuca* was more consistent with Freundlich isotherm, where the high correlation coefficient.

CONCLUSION

The result of this study indicate that the biomass of *Ulva lactuca* is suitable for the development of an efficient metal removal system for the removal of Cu²⁺, Ni²⁺ and Mn²⁺ from the aqueous solution. Biosorption of these metals on the algal biomass was pH dependent and the maximum biosorption was obtained at pH 5.0. The adsorption sites on the algal biomass showed a higher affinity for Cu²⁺ compared to Ni²⁺ and Mn²⁺. The experimental data were described by the Freundlich adsorption isotherm model.

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