

Journal of Applicable Chemistry

2013, 2 (6): 1616-1626 (International Peer Reviewed Journal)



Sequestration of Ni, Fe and Al Ions from Synthetic Wastewater using Melia azedarach L. Leaves

Ammara Younas, Zumaira Siddique*, Kiran Aftab, Ayesha Malik, Iftikhar H. Bukhari

*Department of Chemistry, Government College University, Faisalabad-38000, PAKISTAN

Email: zumairagcuf@gmail.com

Received on 25th October and finalized on 29th October 2013

ABSTRACT

Batch experiments were carried out for sequestration of Ni (II), Fe (II) and Al (III) from ternary solution using Melia azedarach L. leaves (MAL) and Melia azedarach L. leaves ash (MALA). Physicochemical analysis as pH, biosorbent dose, shaking speed, presence of co-ions, contact time and initial metal ions concentration were investigated and optimized. The maximum adsorption efficiencies were 96, 98 and 92.75% for nickel, iron and aluminum ions, respectively at optimized conditions. The presence of co-ions reduced the percentage sorption of metal ions but the effect of anions (~3-5%) was less than that of cations (~8-10%). Freundlich isotherm was best fitted for MAL and Langmuir isotherm for MALA having regression coefficients greater than 0.99. The pseudo second order model was best applicable to all systems. FTIR spectra showed the significant contribution of C-C stretching of aliphatic and aromatic ring and –CN group in MAL and MALA during biosorption phenomenon. The scanning electron micrograph depicted the surface adherence of Ni (II), Fe (II) and Al (III). Batch biosorption assays implemented to real industrial effluents showed the percentage removal of 67, 71 and 77 on MAL and 94, 83 and 86 on MALA for Ni, Fe and Al, respectively.

Keywords: *Melia azedarach* L.Leaves, Freundlich adsorption isotherm, Langmuir adsorption isotherm, Pseudo second order kinetic model, Scanning electron microscopy.

INTRODUCTION

The enhanced level of industrialization and urbanization has significantly increased the discharge of industrial waste water and domestic wastes leading to the degradation of aquatic environments. As a result, a considerable amount of heavy metals is being deposited into ecosystems. It has also increased the biological cycling of toxic heavy metals [1]. Industrial wastes containing synthetic organic compounds and heavy metals are among the most dangerous residues. Heavy metals are assimilated into the food chain and therefore accumulated in the ecosystem [2]. Heavy metals present in the industrial effluents remain as alarming pollutants due to their nondestructive nature, toxicity bioaccumulation and subsequent biomagnifications [3].

The main threats to human health from heavy metals are associated with exposure to lead, cadmium, zinc, mercury, copper, nickel, iron, arsenic, manganese, cobalt and aluminum. Nickel, iron and aluminum are essential elements for human lives and according to WHO, 2003 their permissible limits are 0.02, 0.3 and

0.2 mg L⁻¹, respectively in drinking water. Apart from these limits these metals are toxic in both elemental as well as their chemically combined forms. Exposure to these contaminants present even in low concentrations in the environment can prove to be harmful to the human health as these causes a number of disorders like leucopoenia and lymphopenia by nickel, haemochromatosis by iron and neurological, Bones demineralization and other lethal diseases are caused by aluminium. These metals have been extensively studied and their effects on human health regularly reviewed by international bodies such as the WHO [4]. So, the eradication of these metals from industrial waste water is very essential to minimize their adverse effects [5]. Chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction are common procedures which are used for this purpose. The drawbacks of these methods like partial removal of metal, increased amounts of reagent, energy demands, production of toxic sludge or other waste materials has made it essential to search for an economical method capable of purifying water resources from heavy metals. In this situation a deep interest has been developed towards the novel and financially viable technologies [6]. Biosorption is such a low-cost and highly efficient technique which involves the capability of different kinds of inactive and dead biomasses (microbial biomasses, seaweeds,

agro-industrial wastes) to bind and concentrate heavy metals even in very dilute aqueous systems [7]. It is necessary to have low-cost materials to treat large volumes of waste water. Natural waste materials are available in large quantities and may have potential as sorbents due to physico-chemical characteristics. The sorbent cost is very important to be considered for its use and it should be easily available. The use of natural adsorbents from agricultural and forest wastes have been reported in literature. Biosorbents of plant origin are mainly agricultural by-products, such as maize cob and husk, sunflower stalk, medicago sativa, cassava waste, wild cocoyam, sago waste, peanut skins, shea butter seed husks, banana pith, coconut fiber, sugar-beet pulp, wheat bran, sugarcane bagasse [8]. In the present study, leaves and ash of *Melia azedarach* L. were used as biosorbents for sequestration of toxic metals from ternary solution. This plant is abundantly available in India, Pakistan and other countries.

Hence, the present paper aims at evaluating the adsorption efficiencies of toxic metals using nonconventional and low-cost material as biosorbent. The effect of various parameters namely pH, adsorbent dose, shaking speed, presence of co-ions, contact time and initial metal concentration on the removal of toxic metals (Ni, Fe and Al) had been investigated. The kinetics of metal adsorption by MAL and MALA was analyzed by various kinetic models. Experimental equilibrium data were fitted to the Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins isotherm equations to determine the bestfit isothermal model and then batch adsorption process was applied to industrial effluents.

MATERIALS AND METHODS

Leaves and ash of *Melia azedarach* L. were used as biosorbents in the experiments. The leaves were washed with distilled water, dried, crushed and stored. Ash was prepared by burning leaves. All chemicals used were of analytical grade. A ternary stock solution (1000 mg L^{-1}) of metal ions (Ni, Fe and Al) was prepared by dissolving nickel chloride, ferrous sulphate and aluminium chloride in distilled water and diluted using distilled water to obtain the working solutions of desired concentration. pH of the solutions was adjusted using HNO₃/ NaOH (0.1 M).

Batch Adsorption Experiment: The batch biosorption experiments were carried out in Erlenmeyer flasks using 0.03 g biosorbent (MAL or MALA) to 30 mL ternary solution containing 25 mg L⁻¹ of all toxic metal ions (Ni (II), Fe (II) and Al (III)) and the mixtures were agitated at 250 rpm speed on a shaker for 60 minutes at 25 °C to reach the sorption equilibrium. Then the contents of the flasks were separated by using centrifuge.

Determination of Metal Ions in Solutions: The residual metal ion concentration was determined by flame atomic absorption spectrophotometer (HITACHI Polarized Zeeman Atomic Absorption Spectrometer) equipped with an air-acetylene burner. The analytical wavelength used for nickel, iron and aluminum ions was 232, 248.3 and 256.8 nm, respectively.

FTIR Analysis: FTIR studies were carried out to understand the binding mechanism of sorption and to identify the functional groups present on the biomass surface. FTIR spectrometer of IR prestige-21

SHIMADZU Company Japan within range of 4000-400 cm⁻¹ was used. All analysis was performed using KBr pellets as back ground material. 0.03 g KBr was pressed with 0.03 g of loaded and unloaded biosorbent under high pressure to form a pellet.

SEM Analysis: The surface structure and particle size distribution of biosorbent was examined using Scanning Electron Microscope of model S-2380N of HITACHI Company Japan. The non prepared metal loaded and unloaded samples were analyzed at 1×10^{-2} torr operating pressure.

RESULTS AND DISCUSSION

Effect of pH: A number of studies on biosorption have been recognized that pH greatly affects the binding ability of metal ions in the sorption process. In the present work, the influence of pH on biosorption efficiencies was reported in the range of 1 to 7. 0.03 g biomass was dispersed in 30 mL of the solution containing 25 mg L^{-1} of each metal concentration. All flasks were maintained at different pH values ranging from 1 to 7 and were shaken at the speed of 250 rpm for 60 minutes. The removal efficiencies were found to increase with increasing pH of the solution and the maximum removal efficiency was observed at pH 4.0 for both MAL and MALA.

The removal efficiencies were 80, 78.8 and 74.89% for Fe (II), Ni (II) and Al (III) using MAL and 87, 81.67 and 85.5% for Ni (II), Fe (II) and Al (III) using MALA, respectively. However, further increase in the pH value from 4.0 through 7.0 resulted in decrease in biosorption capacity as depicted in fig.1.

Less adsorption capacity at low pH is result of the protonation of solution which leads to a competition between metal and H^+ ions. Enhanced adsorption with increasing pH from 2 to 4 suggests that adsorbent's surface became more negatively charged. As a result the electrostatic attraction forces become more prominent and so, cationic metal ion adsorption is increased [9].



Figure.1Effect of pH on the sequestration of Ni(\blacklozenge), Fe(\blacksquare) and Al(\blacktriangle) using MAL (—) and MALA (...) (W = 0.03 g, C_i = 25 mg L⁻¹, V = 30 mL, agitation speed = 250 rpm, contact time = 60 minutes)

Effect of Biomass Dose: Biomass dosage is an important factor that affects the efficiency and the amount of metal adsorbed per unit mass of biosorbent. Various amounts ranging from 0.03 to 0.21 g of MAL and MALA were taken into flasks containing 30 mL solution of 25 mg L^{-1} concentration. The flasks were agitated at 250 rpm speed for 60 minutes and sorption was observed at fixed pH 4.

The *Melia azedarach* L. leaves showed the maximum removal of 88.15, 82.5 and 69.21% for Fe (II), Al (III) and Ni (II), respectively (fig.2). Increase in biomass concentration increased the level of biosorption due to the overall increase in surface area of the biomass leading to an increase in the number of binding sites [10]. Maximum uptake was attained at 0.09 g of MAL biosorbent on further increase in pulp density decline in adsorption process was noticed.

In case of MALA the maximum removal efficiency (95, 90.9 and 92.75%) of Fe (II), Ni (II) and Al (III), respectively was observed at 0.03 g of biomass in 30 mL of solution. *Melia azedarach* L. ash was more efficient biosorbent than MAL as it shows maximum removal at very small quantity due to fine particles that provided larger surface area for the eradication of metal ions. This may be presumed that at higher adsorbent dosage the interaction between adsorbent-adsorbent particles increases than adsorbent-adsorbate particles. This interaction between particles of adsorbent may lead to aggregation of adsorbent which reduces the total available surface area resulting in decreased adsorption [11].



Figure 2.Effect of biosorbent dose on the sequestration of Ni(\blacklozenge), Fe(\blacksquare) and Al(\blacktriangle) using MAL (—) and MALA (…) (pH = 4.0, C_i = 25 mg L⁻¹, V = 30 mL, agitation speed = 250 rpm, contact time = 60 minutes)

Effect of Shaking Speed: Shaking speed greatly affects the removal efficiency as energy is consumed in this process. So, optimization of shaking speed is also essential to evaluate a sorption process. To optimize the agitation speed experiment was carried out by taking 7 flasks containing 30 mL of 25 mg L^{-1} ternary solution. Optimum amount of biomass was added and were placed on orbital shaker at different speeds of agitation (50, 100, 150, 200, 250 and 300 rpm) for 60 minutes.

The highest removal efficiencies were attained at speed of 250 rpm. The values were 59, 63, and 65% for Ni (II), Fe (II) and Al (III) on MAL and 69, 71 and 65% on MALA, respectively. At 50 rpm the Ni, Fe and Al ions showed lowest sorption and as the shaking speed increased, the amount of sorbed metal ions also increased up to 250 rpm (fig.3). The adsorption capacity declined slightly when the agitation was further increased to 300 rpm.

On shaking, the solid particles in the solution move quickly and a large number of metal ions migrate towards the surface of adsorbent. It results in increase of external mass transfer speed of the metals and equilibrium was established more quickly. However, further increase in the shaking speed decreased the diffusion rate. Extra energy of high shaking speed smashed the newly formed linkage of sorbate and sorbent [12].



Figure 3.Effect of shaking speed on the sequestration of Ni(\blacklozenge), Fe(\blacksquare) and Al(\blacktriangle) using MAL (—) and MALA (…) (pH = 4.0, W =0.09 g for MAL and 0.03 g for MALA, C_i = 25 mg L⁻¹, V = 30 mL, contact time = 60 minutes)

Effect of Co-ions: In wastewaters the presence of cations and anions may cause synergistic or antagonistic interactions. Therefore, the competitive effect becomes important in the polluted water treatment applications. The existence of other metal ions results in the chemical interactions between metal ions and competition for the active sites. This competition results in the decrease of biosorption capacity [13].

The effect of competitive ions (Na⁺¹, Mg⁺², Cl⁻¹ and SO₄⁻²) on the sequestration of Ni (II), Fe (II) and Al (III) ions by MAL and MALA was studied (Fig. 4 & 5). The results indicated that the removal efficiencies of Ni (II), Fe (II) and Al (III) ions were greatly reduced in the presence of cations as compared to anions. The reduced binding capacities were result of competition for binding sites and by the increased concentration of metal ions in solution, which reduces mobility of the ions in solution. Anions have less impact on the biosorption process because the surface of the adsorbent is negatively charged and there is no competition between these ions and metals for the adsorption. The results represent that less reduction occurs in the values of percentage removal in case of MALA as compared to MAL.



Figure 4.Effect of cations on the sequestration of Ni(\blacklozenge), Fe(\diamondsuit) and Al(\diamondsuit) using MAL (—) and MALA (…) (pH = 4.0, W = 0.09 g for MAL and 0.03 g for MALA, C_i = 25 mg L⁻¹, V = 30 mL, agitation speed = 250 rpm, contact time = 60 minutes)



Figure 5. Effect of anions on the sequestration of Ni(\blacklozenge), Fe(\diamondsuit) and Al(\diamondsuit) using MAL (—) and MALA (…) (pH = 4.0, W = 0.09 g for MAL and 0.03 g for MALA, C_i = 25 mg L⁻¹, V = 30 mL, agitation speed = 250 rpm, contact time = 60 minutes)

Sorption Kinetic Studies: Equilibrium time is a significant parameter that influences the biosorption process. The removal efficiencies of metal ions in the solution were found to be enhanced with time and after reaching the equilibrium it was remained constant. In adsorption experiments using MAL, Fe (II) ions had the maximum percent removal of 88.87% at the end of 40 minutes, followed by Al (III) and Ni (II) ions with 65.5 and 57.34%, respectively. The highest biosorption efficiencies using MALA were 98.5 and 92.5 for Fe (II) and Ni (II), respectively at contact time of 40 minutes. For Al (III) equilibrium was established after 20 minutes and maximum removal efficiency was 96% for it. At the start, the rapid increase in adsorption was due to availability of large surface area that provides more active sites for attaching metals. After that the binding sites of biosorbent were exhausted rapidly and removal capabilities become insignificant. Such type of sorption mechanism has been widely studied in literature which comprises of two stages. First one is rapid and significant and second is slow and less important [14].

The kinetic studies of biosorption processes give information about reaction pathway along time to establish equilibrium. Pseudo-first order, Pseudo-second order, Elovich equation and Intra-particle diffusion models were applied on experimental data (table1).

For pseudo-first order kinetic model the correlation coefficient values were less than 0.99 and the experimental q_e values (12.34-39.57 mg g⁻¹) for Ni (II), Fe (II) and Al (III) on MAL and MALA, respectively disagreed with the calculated ones (1.038-5.083 mg g⁻¹). So, these values indicated that the following process was not well fitted with first-order kinetics.

The tabulated values showed a good union between experimental " q_e " (12.34-39.57 mg g⁻¹) and calculated " q_e " (10.41-39.22 mg g⁻¹) values in case of pseudo second order kinetic model with high correlation coefficient (0.99) value. It is recommended that this sorption process follows the chemisorptions. The pseudo-second order kinetic equation was used to find out the equilibrium sorption capacity, rate constants and initial sorption rate for a process. This equation has successful application in the adsorption of metal ions, herbicides, dyes, oils and organic substances from aqueous solutions [15, 16].

The validity of the Elovich equation and Intra-particle diffusion model to the biosorption process was also experienced. The parameters initial sorption rate " α " and desorption rate constant " β " are tabulated in Table 1. The regression constants of both models are less than 0.99 showing that this adsorption process does not follow the Elovich equation and Intra-particle diffusion model.

Models	Kinetic	Ni	Fe	Al	Ni	Fe	Al
	Parameters		MAL			MALA	
Pseudo-	\mathbb{R}^2	0.05	0.12	0.74	0.55	0.79	0.77
first order	$q_{e} (mg g^{-1})$	2.06	1.04	5.08	0.55	1.37	1.02
	$K(\min^{-1})$	0.00	0.00	0.03	0.04	0.03	0.03
Pseudo-	\mathbf{R}^2	0.99	0.99	0.99	0.99	0.99	0.99
second	$q_{e} (mg g^{-1})$	10.40	17.00	39.21	19.31	19.69	18.48
order	$h_0 (g mg^{-1} min^{-1})$	17.77	19.60	57.47	49.26	53.76	93.46
	K_2 (g mg ⁻¹ min ⁻¹)	0.16	0.67	0.04	0.13	0.14	0.27
Elovich	R^2	0.12	0.37	0.92	0.90	0.80	0.79
equation	$\alpha (\text{mg g}^{-1} \text{min}^{-1})$	6.34×10^{22}	7.34×10^{28}	4.5×10^{7}	1.76×10^{23}	6.15×10^{25}	4.17×10^{29}
1	$\beta (\text{mg g}^{-1} \text{min}^{-1})$	5.43	4.19	0.54	3.08	3.32	3.99
Intra-	\mathbf{R}^2	0.09	0.24	0.78	0.88	0.83	0.66
narticle	\mathbf{K}_{1} (mg g ⁻¹ min ^{1/2})	0.08	0.09	0.86	0.00	0.15	0.00
diffusion	$C (mg g^{-1})$	10.09	16.38	32.14	17.86	18.31	17.55

Table 1. Kinetic parameters of toxic metals using MAL and MALA

Adsorption Isotherms: The feasibility and efficiency of a biosorption process depends not only on the properties of the biosorbent but also on the concentration of the metal ion in solution. The equilibrium sorption efficiency decreased from 58.8-44.24% for Ni(II), 67.4-57.92% for Fe (II) and 46.8-35.48% for Al (III) at initial concentrations of 5-25 mg L⁻¹, respectively for MAL. For MALA these values were 91-38% for Ni (II), 88.6-43.32 for Fe (II) and 79.6-43.08 for Al (III), respectively.

Adsorption isotherm is an important tool that indicates relative affinities of biosorbents for a particular metal. It also helps in understanding the type of interaction that takes place between metal ions and adsorbent surface such as physical adsorption, nucleation or multilayer adsorption. The five most common adsorption isothermal models (Langmuir, Freundlich, Temkin, Dubinin-Radushkevich and Flory-Huggins) were used to analyze the equilibrium adsorption data. Among these Freundlich isotherm model was the most favorable model for MAL with R^2 values (>0.99). K_F is Freundlich constant that denotes capacity of adsorption by heterogeneous sites having varying energy levels and n is the intensity between adsorbate and adsorbent. Its values lies between 1 and 10 represent beneficial adsorption [17]. According to Table 2 the values of n were found to be greater than unity for systems using MAL adsorbent. Whereas, a value below unity implies chemisorptions process where n above one is an indicative of cooperative adsorption.

The sorption data of MALA showed the good fit on Langmuir isotherm with high value of regression coefficients (R^2). The linear isotherm constants q_m , b and are presented in Table 2. The good placement of equilibrium data for Langmuir expression helps in confirmation of monolayer coverage of toxic metals onto biosorbents. The adsorption constant b was related to the attraction for active sites and lower value of b indicated that the particles radius of biosorbent was small toward adsorption. The separation factors R_L obtained in the present study was in the range of 0 to 1, describing that the biosorption process was favorable.

The sorption data was analyzed in accordance with the linear form of the Temkin, Dubinin-Radushkevich and Flory-Huggins isotherm. However, the following sorption data had not any correlation as well with these three equations as Langmuir and Freundlich models proved by the regression coefficients values as mentioned in table 2.

Models	Isothermal	Ni	Fe	Al	Ni	Fe	Al
	parameters	MAL			MALA		
Freundlich	R^2	0.99	0.99	0.99	0.92	0.96	0.81
isotherm	n (L mg ⁻¹)	1.04	1.07	1.02	0.23	0.26	0.34
	K_{f} (mg g ⁻¹)	0.27	0.28	0.36	5.70	5.14	4.68
Langmuir	R^2	0.99	0.98	0.89	0.99	0.96	0.98
isotherm	$q_m (mg g^{-1})$	10.54	11.46	6.97	10.03	10.95	11.42
	b (L mg ⁻¹)	0.04	0.07	0.04	1.68	0.08	0.66
Temkin	\mathbf{R}^2	0.90	0.94	0.92	0.92	0.92	0.84
isotherm	$A_T (dm^3 mmol^{-1})$	0.56	0.71	0.63	45.55	19.26	7.99
	$B_T (kJ mg^{-1})$	1.34	1.74	2.07	1.56	1.37	1.06
D-R isotherm	\mathbf{R}^2	0.95	0.95	0.93	0.93	0.90	0.95
	$q_d (mg g^{-1})$	5.07	4.00	3.39	11.71	9.79	11.88
	$B_D (mol^2 kJ^{-1})$	0.00	0.00	0.00	0.00	0.00	0.00
	E_D (kJ mol ⁻¹)	20.41	22.37	22.37	31.47	50	40.82
F-H isotherm	\mathbf{R}^2	0.66	0.97	0.97	0.98	0.98	0.99
	K _{FH}	0.35	0.28	0.46	0.13	0.15	0.18
	$\Delta G_{o}(kJ mol^{-1})$	-1.09	-1.33	-8.26	-2.12	-2.02	-1.82
	α_{FH}	-0.14	-0.13	-0.09	-0.44	-0.41	-0.33

Table 2. Equilibrium isothermal parameters of toxic metals using MAL and MALA

Characterization of Biosorbent Materials

SEM Analysis: The morphological characteristics of biosorbents were evaluated using scanning electron microscopy. Scanning electron micrographs clearly revealed the surface texture and morphology of the biomass (MAL, MALA) before and after biosorption of Ni, Fe and Al ions (fig. 6). Many different pores and irregular particles were present on the grooved surface of unloaded biomass that makes the surface of biomass rough. SEM analysis confirms the accumulation of metal ions on biomass surfaces after biosorption. The pores of the MAL and MALA surface were filled up by metal ions and the surface had become smooth. Similar SEM observations were reported by other researchers [18, 19].



Figure 6.Scanning electron micrograph of MAL and MALA (a,c) before and (b,d) after toxic metals biosorption

FTIR Analysis: FTIR spectroscopy (4000-400 cm⁻¹) gives valuable information about the bonding nature and allows identification of functional sites such as carbonyl, cyanide, hydroxyl and ether groups on the cell surface. The various functional groups were responsible for biosorption of metals (Ni, Fe and Al) ions by *Melia azedarach* L. leaves and ash. Table 3 presented the functional groups and IR frequencies of MAL and MALA involved in biosorption phenomenon. The difference in peak intensities before and after biosorption proved the formation of new bonds. It was also seen that several new bands in the finger print region appeared after biosorption indicating that some new linkages are formed. These peaks showed the presence of halogens compounds.

		MAL and MALA using FTIR spectroscopy					
Sr. No.	Functional groups	Absorption frequencies (cm ⁻¹)					
		Native MAL	Loaded MAL	Difference	Native MALA	Loaded MALA	Difference
1	O-H str.	3271	3265	6	-	-	-
2	C-H str.	2929	2929	0	2991	2978	13
3	C-N	2347	2341	6	2339	2318	21
4	C-C str.	2156	2131	25	-	-	-
5	C-0	-	-	-	1791	1788	3
6	Aromatic	1587	1531	56	1467	1452	15
7	C-H str. (Alkenes)	1425	1433	8	-	-	-
8	Ar-O str.	1253	1244	9	1259	1253	6
9	R-O str.	1053	1039	14	1041	1049	8
10	Ar-H str. Out of plane	-	-	-	875	875	0
11	C-Br	-	-	-	596	596	0

Table 3 . Characteristic absorption frequencies of functional groups of
MAL and MALA using FTIR spectroscopy

APPLICATIONS

Spiking of Metal Ions: The samples collected from industries were analyzed for three metal ions (Ni, Fe and Al) before and after spiking. Then the samples were exposed to biosorbents (MAL and MALA) at optimized conditions for examining the adsorption of metals on their surface. The concentration of remaining metals after biosorption was determined by flame atomic absorption spectrophotometer. It was clearly indicated from the results that *Melia azedarach* L. leaves and ash are very efficient biosorbents for the abolition of toxic metals from wastewater. MALA is more proficient adsorbent as compared to MAL as its removal efficiencies were in the range of 74.6-94% for metals of industrial effluents. MAL has removal capacities in the range of 60-77% for these samples. The results are integrated in the form of Fig. 7 from which comparable capabilities of MAL and MALA could be recognized to eliminate metals from industrial effluents. The initial concentrations of Ni (II), Fe (II) and Al (III) are taken as control. It shows that no sorption has occurred because biosorbent is not added in these samples.



Figure 7. Sequestration of toxic metals from three industrial samples

Sample no.	Type of metal	Before Spiking	After spiking	Using MAL	Using MALA
	Ni (II)	0.44	5.44	1.8	0.68
Sample 1	Fe (II)	0.86	5.86	1.98	1.09
	Al (III)	0.00	5.00	1.46	0.79
	Ni (II)	0.44	5.44	1.93	0.32
Sample 2	Fe (II)	0.09	5.09	1.45	0.87
	Al (III)	0.82	5.82	1.32	0.78
	Ni (II)	0.34	5.34	1.94	0.53
Sample 3	Fe (II)	0.68	5.68	2.12	0.98
	Al (III)	0.51	5.51	2.18	1.4

 Table 4. Analysis of different industrial effluent

CONCLUSIONS

The plant *Melia azedarach* L. commonly called China-berry is abundantly available plant especially in India and Pakistan. In this study, *Melia azedarach* L. leaves and their ash are found to be a good adsorbent for the removal of Ni (II), Fe (II) and Al (III) from aqueous solutions. In conclusion, the data has shown that, the sorption process of toxic metals on both biomasses was feasible and spontaneous in nature. The kinetics of the all sorption systems followed pseudo-second order model. Among the five adsorption isotherms tested, it was found that the adsorption data for metal ions on MAL was better fitted to Freundlich while that of using MALA was fitted to Langmuir adsorption model. Hence, biosorption of metals on MAL biosorbent was a multilayer sorption process while that of MALA was a monolayer sorption process.

ACKNOWLEDGEMENTS

This work is the part of M.phil work done by Ammara Younas under the supervision of Zumaira Siddique. Authors are thankful to Hi- tech lab, University of Sargodha for generous support and technical assistance.

REFERENCES

- [1] J. C. Onwuka, V. O. Ajibola, J. A. Kagbu, A. J. Manji, Arch. App. Sci. Res. 2011, 3, 191-207.
- [2] S. C. Rocha, C. J. De-Assis, M. G. Da-Sila, P. C. Gonclaves, *Environ. Technol.* 2006, 27, 979-990.
- [3] P. L. Iynengar, C. Vekobachar, J. Ind. Microb. Biotechnol. 2000, 25, 1-7.
- [4] J. Lars, Brit. Med. Bull. 2003, 68, 167-182.
- [5] A. Hmetsar, J. Hazard. Mat. 2008, 157, 448-454.
- [6] C. Lamaia, M. Kruatrachuea, Sci. Asia. 2005, 31, 121-127.
- [7] S. S. Ahluwalia, D. Goyal, *Biores. Technol.* **2007**, 98, 2243–2257.
- [8] A. U. Augustine, J. N. Egila, Int. J. Mod. Chem. 2013, 4, 167-179.
- [9] A. C. John, O. Lara, A. Victor, O. Oladunni, Am-Eurasian J. Sci. Res. 2011, 6, 123-130.
- [10] S. Pattabhi, S. Madhavakrishan, K. Manickavasagam, K. Rasppan, R. Venekatesh, P. S. S. Shabudeen, *Electron. J. Chem.* **2008**, 5, 761-769.
- [11] L. C. Overah, J. Appl. Sci. Environ. Manage. 2011, 15, 87-95.
- [12] N. Jamil, M. A. Munawar, S. Badar, Sidra-tul-Muntaha, J. Chem. Soc. Pak. 2009, 31, 362-370.
- [13] F. A. Abu Al-Rub, M. H. El-Naas, I. Ashour, M. Al-Marzouqi, *Biochem. Process.* 2006, 41, 457-464.
- [14] A. Saeed, M. W. Akhter, M. Iqbal, Sep. Pur. Technol. 2005, 45, 25-31.
- [15] B. H. Hameed, J. Hazard. Mat. 2008, 154, 204-212.
- [16] B. H. Hameed, D. K. Mahmoud, A. L. Ahmad, J. Hazard. Mat. 2008, 158, 65-72.
- [17] K. Kadirvelu, C. Namasivayam, *Environ. Technol.* **2000**, 21, 1091-1097.
- [18] M. Shakirullah, Habib-ur-Rehman, I. Ahmad, S. Shah, Hameedullah, J. Chin. Chem. Soc. 2006, 53, 1045-1052.
- [19] A. Wilke, R. Buchholz, G. Bunke, *Environ. Biotechnol.* 2006, 2, 47-56.