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Full Length Research Paper

Removal of heavy metals from aqueous solution by using mango biomass

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Biosorbent and unfertilizable flowering buds of mango plant, a local agrowaste in Multan, Pakistan known as battoor is used in this study. Efficacy of the biosorbent is tested in batch for Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} in single metal solution under control experimental conditions. The concentration of the biomass was 0.5 g. Metal ions were analyzed by atomic absorption spectrophotometer using its specific lamp for each metal at a specific wavelength. It was found that metal sorption increases when the equilibrium metal concentration is raised. Uptake sorption in single metal system (SMS) were 24.4 mg Pb^{2+}, 22.506 mg Cu^{2+}, 18.932 mg Zn^{2+} and 17.618 mg Ni^{2+} per gram for *Mangifera* sp. (mango) biomass at the highest experimental solution concentration, which is 150 mgl^{-1}. Removal of metal were 92% Pb^{2+}, 86.84% Cu^{2+}, 83.96% Zn^{2+}, 82.29% Ni^{2+} for *Mangifera sp.* (mango) biomass at the lowest experimental solution concentration, that is, 25 mgl^{-1}. Biosorption equilibrium isotherms were plotted for the metal uptake q against the residual metal concentrations in solution. The q versus C_f sorption isotherm relationship was mathematically expressed by linear Langmuir and Freundlich models. The values of separation factor or equilibrium parameter between 0 and 1 indicate the favorable sorption for four tested metal on the biosorbent. Values of surface coverage approach nearly 1 with the increasing solution concentration which indicate the effectiveness of the biosorbent under invesigation.The non-living biomass of *Mangifera* sp. present comparable biosorption capacity for Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} ions with other types (sources) of biosorbent materials found in previous literature. Efficiency of the biomass indicates that they are effective in removing metal ions from single metal solutions as well as other co-ions with the main metal of solution.

Key Words: *Mangifera* sp., biosorbent, intercationic, efficacy.

INTRODUCTION

Water is necessary for the existence of life on earth. 75% of the earth is covered with water out of which 97% is saltish and only 3% is available for drinking, agriculture, domestic and industrial consumption, while the rest is locked up in oceans as salt water, polar ice caps, glaciers and underground reservoirs. Due to increase in industrialization and human population, demands for water supply have also been increased but considerable part of this limited quantity of water is by sewage, industrial wastes and a wide variety of synthetic chemicals (Dara, 1998). The major sources of water contamination are domestic, industrial and agricultural as well as solid waste pollution, thermal pollution, shipping water pollution and radioactive wastes (Tyagi and Mehra, 1994).

Heavy metals such as zinc, lead and chromium have a number of applications in basic engineering works, paper and pulp industries, leather tanning, organochemicals, petro-chemicals, fertilizers, etc (Trivedi, 1987) and these industries are the main sources of heavy metals in the environment.

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Abbreviations: SMS, Single metal system; **DDW,** doubled distilled water; **BMS,** binary metal system.

Rapid industrialization and technological development enhance the concentration of heavy metals, posing a significant threat to environment and public health because of their toxicity, accumulation in the food chain and persistence in nature (Ceribasi and Yetis, 2001).

Over a few decades, several chemical methods have been devised for the treatment and removal of heavy metals. The commonly used procedures for removing metal ions from aqueous streams include phyto-remediation, chemical precipitation, lime coagulation, ion exchange, reverse osmosis and solvent extraction (Rich and Cherry, 1987). But the disadvantages like incomplete metal removal, high reagent and energy requirements, generation of toxic sludge or other waste products that require careful disposal has made these methods comparatively cost effective for removing heavy metals from aqueous effluents (Ahalya et al., 2003).

The search for new technologies involving the toxic metals from waste waters has directed attention to biosorption based on metal binding capacities of various biological materials. Biosorption is considered to be a fast physico-chemical process. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normal water) containing dissolved species to be sorbed (sorbate, metal ions) due to higher affinity of biosorbent for the sorbate species, which was later attracted and bound there by different mechanisms (Kratochvil and Volesky, 1998). Different parameters may affect the biosorption mechanism to various extents (Gadd, 2009). pH is the most important parameter that can affect the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions (Galun et al., 1983). Temperature normally has no effects on biosorption performances in the range of 20 - 35℃ (Asku, 1992). Biomass concentration in solution seems to influence specific uptake. For lower values of biomass concentrations, there is an increase in the specific uptake (Fourest and Roux, 1992). Metal affinity to the biomass can be manipulated by pretreating the biomass with alkalis, acids, detergents and heat, which may enhance the amount of the metal sorbed. When non-viable biomass is used in the removal of heavy metals, alkali pretreatment is an effective method to improve the bioabsorption capacity for metal ions (Yan and Viraraghavan, 2000). Hence, the bioadsorption efficiency of dead biomass may be greater, equivalent to, or less than that of live biomass depending on the pre-treatment method applied. It is necessary to carry out more detailed studies to understand why enhancement or reduction in adsorption capacity occurs under specific pre-treatment conditions.

Biomass is available in large quantities as a waste product and their potential utilization as a metal biosorbent is of interest. Till now, on a large scale, the microbial potential and waste biomass has been exploited. Previous studies on metal biosorption have been restricted to simple solution of only one metal. Masud and Anantharaman (2005) found biosorption activity of copper (II) on negative bacteria *Thiobacillus ferooxidans*, while Anurag et al. (2007) used agrose gel biopolymer for the removal of Cu (II) from aquous system. King et al. (2007) used *Azadirachta indica* bark, while Kalyani et al. (2009) used *Giycyphagus domesticus* shell powder for the removal of zinc from aqueous solution. Pb (II) removal by citrus pectin and *Pseudomonas aeruginosa* were studied by Balaria et al. (2005) and Kang et al. (2008), respectively. Biosorption of Fe (II) from aquous solution on tamarad bark (*Tilletia indica*) and potato peel waste (*Solanum tuberosum*) have been studied by Devi and Abdulsalam (2009), while Ahalya et al. (2005) used Bengal gram husk (husk of channa dal, *Cicer arientinum*) in the biosorption of Fe (III). Biosorption of Ni (II) ions have been investigated by Vijayaraghavan et al. (2006) and Mogollon et al. (1998) onto *Sophora wightii* and filamentous fungi strains *Rhizopus* sp., respectively. Hashim and Chu (2004) studied the binding ability of Cd (II) on seven different species of brown, red and green seeweeds while Tangaromsuk et al. (2002) studied the Cd (II) removal on living cell gram-negative bacterium, *Sphingomonas paucimobilis*.

The objective of this study is to develop an inexpensive and effective biosorbent that is easily available in large quantities and feasible economically for multiple metal ions in solution. Biosorbent, unflowering buds (battoor) of mango *Mangifera* sp. is tested for biosorption of multiple metal ions in single and binary metal systems.

MATERIALS AND METHODS

Preparation of biosorbent

Mangifera sp. biomass was collected from orchids of Multan. The biomass was dried in the sun for fifteen days. The buds were removed and further dried in sun for another fifteen days. This biomass was washed with tap water to remove any dust or foreign particles attached to biomass and thoroughly rinsed with distilled water. The washed biomass was dried at 50℃ and ground to powder with kitchen grinder. Grinded biomass was further thoroughly washed with distilled water till the color of washing water is clean. The powdered biomass was dried in oven at 50℃ till a constant weight was attained. The biosorbent was again ground to powder and was sieved with three different sized meshes. Four different grade particle sizes were obtained. First particle size was less then 255 mm, second 255 - 355 mm, third 355 - 500 mm and fourth was 500 - 710 mm. The aforesaid particle size no. 2 was selected for further study because the amount of no. 1 size was lesser, no. 3 and 4 sizes will show less efficiency because of less surface area as compared to the size no. 2.

Stock solutions of metal ions

Stock solution were prepared in doubled distilled water (DDW) from the salts of four metals (Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+}) under investigation. For 1000 mg l^{-1} solution preparation, dried salts of 1.598 g of $Pb(NO_3)_2$, 3.929 g of $CuSO_4.5H_2O$, 3.107 g of $NiSO_4.6H_2O$ and 4.549 g of $Zn(NO_3)_2.6H_2O$ were dissolved in 1000 ml of DDW. The resulting stock solutions were stored in air tight plastic bottle.

Batch studies of single metal system (SMS)

In all sets of experiments, fixed volume of single metal ion solutions(100 ml) of various concentrations in conical flasks of Pyrex made of 100 - 200 ml working volume was thoroughly mixed with 0.5 g of biosorbent dose, size of 255 to 355 micron at 30°C and 100 rpm (revolutions per minute) shaking speed for 12 h. Twelve hours of equilibrium period for sorption experiment were used to ensure equilibrium. The pH range was adjusted from 4 - 6 by using 0.1 M HNO_3 and 0.1M HCl solutions. The flasks were kept on rotating shaker with constant shaking. At the end of the experiment, the flasks were removed and the solution was separated from the biomass by filtration through filter paper.

Batch studies of binary metal system (BMS)

In all sets of experiments, 100 ml volume of BMS solutions with various concentrations (25, 50, 75,100,125 and 150 mgl^{-1}) of main metal and 25 mgl^{-1} can affect metal concentration or co-ion in the same solution in conical flasks of 100 - 200 ml, working volume was thoroughly mixed with biosorbent dose of 0.5 g and size 255 to 355 mm at 30 ± 1°C and 100 rpm shaking speed for 12 h. Twelve hours of equilibrium period for sorption experiment were used to ensure equilibrium. The pH range was adjusted from 4 - 6 by using 0.1 M HNO_3 and 0.1 M HCl solutions. The flasks were kept on rotating shaker with constant shaking. At the end of experiment, the solution was separated from the biomass by filtration through filter paper.

Metal concentration analysis

After various adsorption experiments, samples (taken after specific time intervals) were diluted to 10 or 20 mg l^{-1} as per requirement of experimental analysis, with distilled water for metal ions determination. The samples of metal solutions prior to and after equilibrium of adsorption were taken. After metal concentration analysis, the final concentration was subtracted from the initial concentration in order to find the metal to be sorbed. The metal ions contents in all the samples were determined by flame atomic absorption spectrometry using a Perkin Elmer AAS (Analyst 300).

Calculation of metal uptake

The quality of biosorbent is judged by the metal uptake (biosorption capacity), q. Amount of metal bound by the biosorbent which disappeared from the solution was calculated based on the mass balance for the biosorbent in the system.

$$q = V(C_i - C_f)/S$$

Where, q = Metal ion uptake capacity (mgg^{-1}); C_i = initial concentration of metal in solution before the sorption analysis (mgl^{-1}); C_f = final concentration of metal in solution after the sorption analysis (mgl^{-1}); S = dry weight of biosorbent (g); V = solution volume (L)

The difference between the initial metal ion concentration and final metal ion concentration was assumed to be bound to the biosorbent.

Freundlich and Langmuir model

To characterize the biosorption for single metal component system, Langmuir and Freundlich models were used. The Langmuir model makes assumptions such as monolayer adsorption and constant adsorption energy while the Freundlich model deals with heterogeneous adsorption. Langmuir equation of adsorption is (Volesky, 2003).

$$q = q_{max}\, bC_f \ / \ (1+bC_f)$$

It is linearized to the form

$$1/q = 1/q_{max} + 1/(b.q_{max})\ (C_f)$$

Where, q_{max} and b are the Langmuir constants. The Freundlich equation of adsorption isotherm is (Volesky, 2003)

$$q = K\ (C_f)\ _1{}^{/n}$$

Its linearized form is represented by the equation

$$\log q = \log K + (1/n) \log C_f$$

Where, q is the amount adsorbed per unit mass of adsorbent and C_f is the equilibrium concentration. The plot of log q vs. log C_f is linear and constants K and n is evaluated from slopes and intercepts.

Separation factor (SF)

The shape of the isotherm can be used to predict whether adsorption system is favorable or unfavorable in a batch adsorption system. Accordingly, the essential feature of Langmiur isotherm was expressed in terms of dimensionless constant called the separation factor. It is defined by the following relationship.

$$Sf = 1/(1+bC_i)$$

Surface coverage (θ)

To account for adsorption behavior of the metal ions on the biomass the Langmiur type equation related to surface coverage is used. The equation is expressed as follow:

$$bC_i = \theta/(1-\theta)$$

and

$$\theta = bCi/(1+bC_i)$$

RESULTS AND DISCUSSION

Efficiency of the non conventional biosorbent of plant origin is tested for removal of metal ions Pb^{2+} Cu^{2+} Ni^{2+} and Zn^{2+} from synthetic solutions in single and binary metal solutions.

Single metal system batch sorption study profile

i. Lead biosorption by *Mangifera sp.*

Data in Table 1 reveals the biosorption of Pb^{2+} by

Table 1. Effect of Pb^{2+} concentration on lead removal and uptake capacity by *Mangifera sp.* biosorbent.

Pb^{2+} concentration	Ci (mgL^{-1})	Cf (mgL^{-1})	Ci-Cf	q (mgg^{-1})	% Removal
25	26.01	2.08	23.93	4.786	92.00308
50	48.07	6.65	41.42	8.284	86.16601
75	76.32	12.53	63.79	12.758	83.58229
100	102.21	13.71	88.5	17.7	86.58644
125	122.14	22.16	99.98	19.996	81.85689
150	147.41	25.41	122	24.4	82.76236

Where, C_i = Initial concentration of metal in solution before the sorption analysis (mgl^{-1}); C_f = final concentration of metal in solution after the sorption analysis (mgl^{-1}).

Table 2. Langmiur and Freundlich isotherm parameters for Pb^{2+} on *Mangifera sp.* biosorbent.

Cf (mgL^{-1})	q (mg/g^{-1})	1/Cf	1/q	log Cf	log q
2.08	4.786	0.480769	0.208943	0.318063	0.679973
6.65	8.284	0.150376	0.120715	0.822822	0.91824
12.53	12.758	0.079808	0.078382	1.097951	1.105783
13.71	17.7	0.072939	0.056497	1.137037	1.247973
22.16	19.996	0.045126	0.05001	1.34557	1.300943
25.41	24.4	0.039355	0.040984	1.405005	1.38739

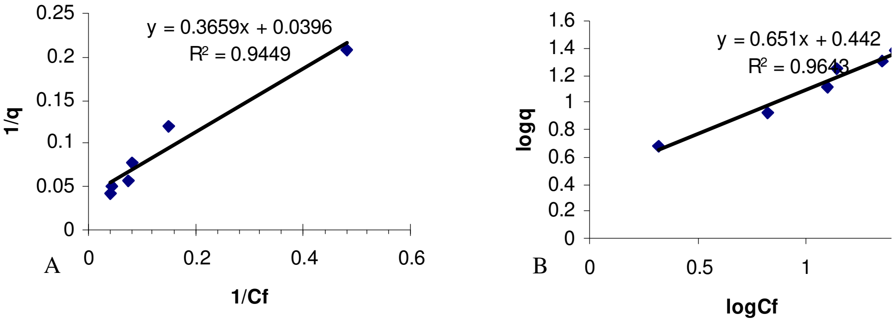


Figure 1. Linearized adsorption isotherm for Pb^{2+} on *Mangifera sp.* biosorbent. A. Langmuir isotherm; B. Freundlich isotherm.

Mangifera sp. biomass as a function of initial concentration of blank solutions. Uptake capacity increases to 24.4 mgg^{-1} and removal of Pb^{2+} from solution is more at low initial concentration, that is, maximum 92.003% at 26.01 mgl^{-1} concentration.

Table 2 shows the Langmiur and Freundlich isotherms parameters of Pb^{2+} biosorption by *Mangifera* sp. biomass and plots in Figure 1 indicate that both models adequately describe the experimental data as the values of coefficient of determination are 0.9449 and 0.9643 for Langmiur and Freundlich isotherms, respectively. Both isotherms model exhibit a good fit to the biosorption data of Pb (II) but Freundlich isotherm model is slightly better than Langmiur isotherm model to fit Pb (II) biosorption data that well cover a concentration range of 25 - 150 mgl^{-1}.

ii. Copper biosorption by *Mangifera sp.*

Table 2 shows the Langmiur and Freundlich isotherms parameters of Cu^{2+} biosorption by *Mangifera* sp. biomass

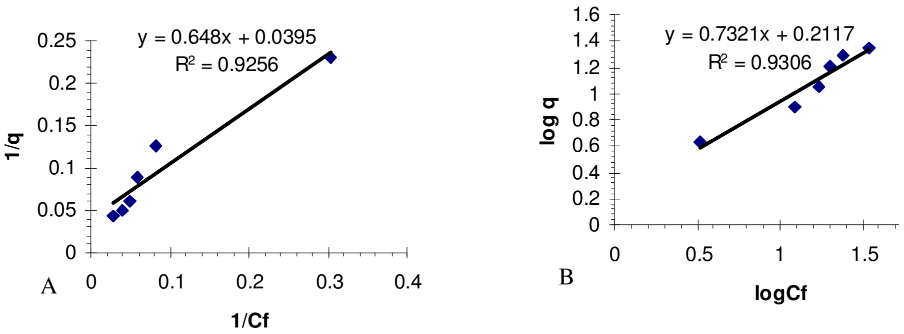


Figure 2. Linearized adsorption isotherm for Cu^{2+} on *Mangifera* sp. biosorbent. A. Langmuir isotherm; B. Freundlich isotherm.

Table 3. Effect of Cu^{2+} concentration on copper removal and uptake capacity by *Mangifera sp.* biosorbent.

Cu^{2+} concentration	Ci (mgL^{-1})	Cf (mgL^{-1})	Ci-Cf	q (mgg^{-1})	% Removal
25	25.01	3.29	21.72	4.344	86.84526
50	52.07	12.3	39.77	7.954	76.37795
75	73.32	17.21	56.11	11.222	76.52755
100	101.51	20.3	81.21	16.242	80.00197
125	123.14	24.3	98.84	19.768	80.26636
150	146.89	34.36	112.53	22.506	76.60835

Table 4. Langmiur and Freundlich isotherm parameter for Cu^{2+} on *Mangifera sp.* biosorbent.

Cf (mgL^{-1})	q (mg/g^{-1})	1/Cf	1/q	log Cf	log q
3.29	4.344	0.303951	0.230203	0.517196	0.63789
12.3	7.954	0.081301	0.125723	1.089905	0.900586
17.21	11.222	0.058106	0.089111	1.235781	1.05007
20.3	16.242	0.049261	0.061569	1.307496	1.21064
24.3	19.768	0.041152	0.050587	1.385606	1.295963
34.36	22.506	0.029104	0.044433	1.536053	1.352298

and plots in Figure 2 indicate that both models adequately describe the experimental data as the values of coefficient of determination are 0.9256 and 0.9306 for Langmuir and Freundlich isotherms, respectively. Both isotherms model exhibit a good fit to the biosorption data of Cu (II) but Freundlich isotherm model is slight better than Langmiur isotherm model to fit Cu (II) biosorption data that well cover a concentration range of 25 -150 mgl $^{-1}$.

iii. Zinc biosorption by *Mangifera* sp.

Table 3 shows Langmiur and Freundlich isotherms parameters of Zn^{2+} biosorption by *Mangifera* sp. biomass and plots in Figure 3 indicate that both models adequately describe the experimental data, as the values of coefficient of determination are 0.9311 and 0.9321 for Langmiur and Freundlich isotherms, respectively. Both isotherms model exhibit a good fit to the biosorption data of Zn (II) but Freundlich isotherm model is slightly better than Langmiur isotherm model to fit Zn (II) biosorption data which covers a concentration range of 25 - 150 mgl $^{-1}$.

iv. Nickel biosorption by *Mangifera* sp.

Table 4 shows the Langmiur and Freundlich isotherms parameters of Ni^{2+} biosorption by *Mangifera* sp. biomass and plots in Figure 4 indicate that both models well describe

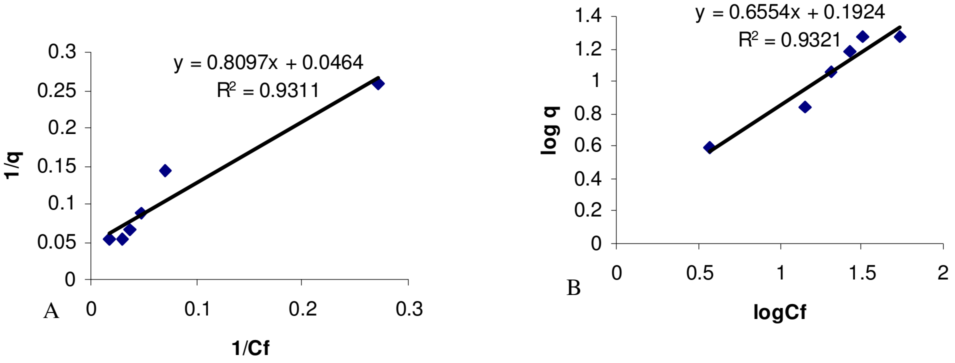


Figure 3. Linearized adsorption isotherm for Zn^{2+}on *Mangifera* sp. biosorbent. A. Langmuir isotherm; B. Freundlich isotherm.

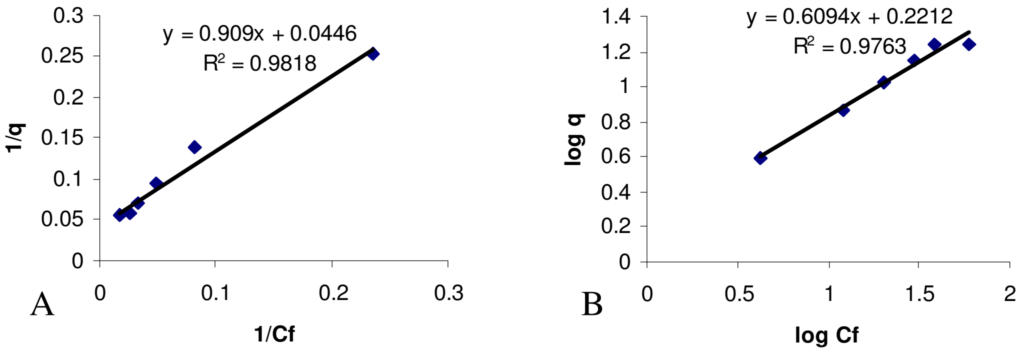


Figure 4. Linearized adsorption isotherm for Ni^{2+} on *Mangifera* sp. Biosorbent. A. Langmuir isotherm; B. Freundlich isotherm.

the experimental data, as the values of coefficient of determination are 0.9818 and 0.9763 for Langmiur and Freundlich isotherms, respectively which is very close to 1 but Langmiur isotherm model is slightly better than Freundlich isotherm model to fit Ni (II) biosorption data which covers a concentration range of 25 - 150 mgl $^{-1}$.

General discussion and comparison of results

The rate of absorption is a function of the initial concentration of metal ions, which makes it an important factor to be considered for effective biosorption (Ahalya et al., 2005). From Figure 5 in general, the data reveal that capacity of biosorbent increases with the initial concentration of metal ions (sorbate). These characteristics represent surface saturation that depends on the initial metal ion concentrations. At low concen-trations, biosorbent sites take up the available metal more quickly. However, at higher concentrations, metal ions need to diffuse to the biomass surface by intraparticle diffusion and greatly hydrolyzed ions will diffuse at a slower rate (Horsefall and Spiff, 2005).

It is found that as metal ions concentration is reduced, biosorption rate reached to higher level and when the metal ions concentration is high, the metal removal rate decreased. Such decline in % removal rate is probably caused by the saturation of some adsorption sites. The results are in agreement with Chen and Wang (2007). The selectivity order for metal ions towards the studied biomass is Pb >Cu >Zn >Ni. This order is same as shown by Zhang (2005) and comparable to Saeed et al. (2005). This differential absorption of metal ions may be ascribed to the difference in their ionic radii. The smaller the ionic radius, the greater its tendency to hydrolyze leading to reduced sorption. The ionic radii of Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} are1.19A°, 0.73A°, 0.74A° and 0.67A°, respectively. The result is similar to previous study by Horsefall and Spiff (2005) and Hanif et al. (2007).

Table 5 give the relationship between absorbed and aqueous concentration at equilibrium. The Langmiur and Freundlich adsorption constants are evaluated from the isotherms with correlation coefficients. Both models represent better absorption process due to high value of correlation coefficients (R^2).

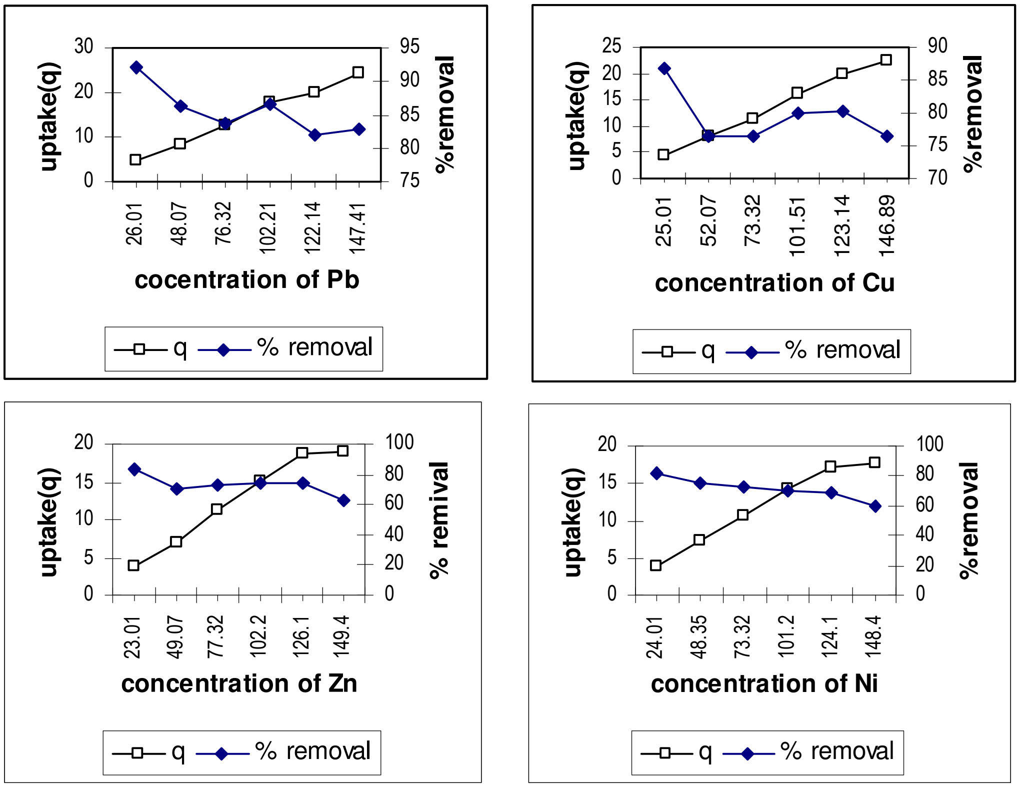


Figure 5. Comparison of uptake capacity (mgg^{-1}) and percentage removal as a function of metal ions concentration by *Mangifera* sp. biosorbent

Table 5. Effect of Zn^{2+}concentration on zinc removal and uptake capacity by *Mangifera sp.* biosorbent.

Zn^{2+} concentration	Ci (mgL^{-1})	Cf (mgl^{-1})	Ci-Cf	q (mgg^{-1})	% Removal
25	23.01	3.69	19.32	3.864	83.96349
50	49.07	14.3	34.77	6.954	70.85796
75	77.32	20.63	56.69	11.338	73.31868
100	102.21	26.85	75.36	15.072	73.73055
125	126.14	32.51	93.63	18.726	74.22705
150	149.41	54.75	94.66	18.932	63.35587

The Langmuir isotherm (1918) considers absorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. The linearized Langmuir equation is:

$$1/q = 1/q_{max} + 1/(b.q_{max})(C_f)$$

Constant b is related to the energy of absorption through the Arrhenius equation. The higher the b, the higher is the affinity of the biosorbent for the metal ions. q_{max} can also be interpreted as the total number of binding sites that are available for biosorption and q as the number of binding sites that are in fact occupied by the metal ions at the concentration C_f (Volesky, 2003).

According to the above data, the affinity order of *Mangifera* sp. biosorbent is Pb > Cu > Zn > Ni. Langmuir isotherm, which represents that monolayer of metal ions (sorbate), is formed on biosorbent. Adsorption-partition constants are determined for metals using the following log form of the Freundlich isotherm:

$$\log q = \log K + (1/n) \log C_f$$

Where, q is the metal ion sorbed (mgg^{-1}), C_f the equilibrium concentration of metal ion solution in mgl^{-1}, K and n are Freundlich constants. The constants K and 1/n

Table 6. Langmiur and Freundlich isotherm parameter for zinc on *Mangifera sp.*biosorbent.

Cf (mgL^{-1})	Q (mg/g^{-1})	1/Cf	1/q	Log Cf	Log q
3.69	3.864	0.271003	0.258799	0.567026	0.587037
14.3	6.954	0.06993	0.143802	1.155336	0.842235
20.63	11.338	0.048473	0.088199	1.314499	1.054536
26.85	15.072	0.037244	0.066348	1.428944	1.178171
32.51	18.726	0.03076	0.053402	1.512017	1.272445
54.75	18.932	0.018265	0.052821	1.738384	1.277196

Table 7. Effect of Ni^{2+} concentration on nickel removal and uptake capacity by *Mangifera sp.* biosorbent.

Ni^{2+} concentration	Ci (mgL^{-1})	Cf (mgL^{-1})	Ci-Cf	q (mgg^{-1})	% Removal
25	24.01	4.25	19.76	3.952	82.29904
50	48.35	12.12	36.23	7.246	74.93278
75	73.32	20.21	53.11	10.622	72.4359
100	101.21	30.15	71.06	14.212	70.21045
125	124.14	38.24	85.9	17.18	69.19607
150	148.41	60.32	88.09	17.618	59.35584

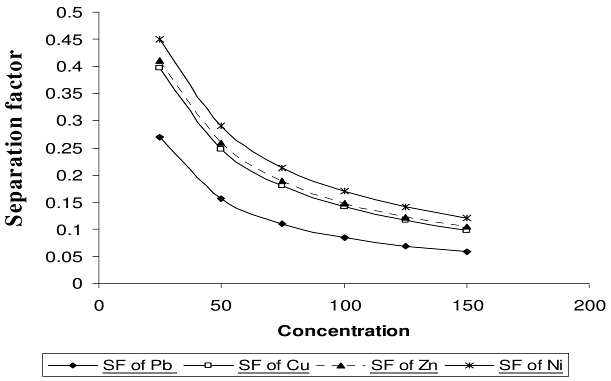


Figure 6. Plot of separation factor (SF) profile for biosorption of $Pb2^{+}$ Cu^{2+} Zn^{2+} and Ni^{2+} on *Mangifera* sp. biomass.

were determined by linear regression from the plot of log q against logC_f. K is a measure of the degree or strength of adsorption. Small value of K indicate the minimal absorption and large value indicates the more absorption (Horsefall and Spiff, 2005) while 1/n is used as an indication ofindication of whether absorption remains constant (at 1/n = 1) or decreases with increasing metal ions concentrations (with 1/n ≠1). The q_{max} value is the maximum value of q and is important to identify the biosorbent highest metal uptake capacity, and as such useful in scale-up considerations (Hanif et al., 2007). The magnitude of the experimental q_{max} for *mangifera* sp. biomass is found to be 24.40, 22.51, 18.93 and 17.62 mgg^{-1} for all the four which are lead copper zinc and nickel metal ions that are comparable with theoretically calculated $q_{max,}$ values from Langmuir and Freundlich isotherm models presented in Table 5. The maximum absorption capacity is observed of lead on *Mangifera* sp.

suggesting that it is a potential biosorbent for removal of lead as well as the other three tested metals.

SF

The shape of the Langmuir isotherm can be used to predict whether a biosorption system is favorable or unfavorable in a batch adsorption process. Accordingly, the essential features of the Langmuir isotherm was expressed in terms of a dimensionless constant called the equilibrium parameter, SF, which is defined by the following relationship:

$$SF = 1/(1 + bCi)$$

Where, SF is the dimensionless equilibrium parameter or separation factor, b, the constant from Langmuir equation and C_i the initial metal ion concentration of 100 mgl^{-1}. The parameter, SF, indicates the shape of the isotherm and nature of the sorption process. SF value between 0 and 1 represents favorable isotherm. The SF values of Pb^{2+} Cu^{2+} Zn^{2+} Ni^{2+} for *Mangifera* sp. biomass is calculated from the equation previously described and plotted against initial metal ion concentration (Figure 6) (Hanif et al., 2007).

Table 6 shows the Langmiur and Freundlich isotherms parameters of Zn^{2+} biosorption by *Mangifera* sp. biomass and plots in Figure 3 indicate that both models adequately describe the experimental data as the values of coefficient of determination are 0.9311 and 0.9321 for Langmiure and Freundlich isotherms, respectively. Table 7

Table 8. Langmiur and Freundlich isotherm parameter for Ni^{2+}on *Mangifera sp.* biosorbent.

Cf (mgL^{-1})	q (mg/g^{-1})	1/Cf	1/q	log Cf	log q
4.25	3.952	0.235294	0.253036	0.628389	0.596817
12.12	7.246	0.082508	0.138007	1.083503	0.860098
20.21	10.622	0.04948	0.094144	1.305566	1.026206
30.15	14.212	0.033167	0.070363	1.479287	1.152655
38.24	17.18	0.026151	0.058207	1.582518	1.235023
60.32	17.618	0.016578	0.05676	1.780461	1.245957

Table 9. Comparison of Langmuir and Freundlich isotherm for lead, copper, zinc and nickel by *Mangifera sp.* biosorbent.

Metals	Langmuir isotherm parameters			Experimental value	Freundlich isotherm parameters			
	q_{max}	b	R^2	q_{max}	q_{max}	K	1/n	R^2
Pb	25.25	0.108	0.9449	24.40	22.73	2.767	0.6510	0.9643
Cu	25.31	0.0609	0.9256	22.51	21.68	1.628	0.7321	0.9306
Zn	21.55	0.0573	0.9311	18.93	21.46	1.557	0.6554	0.9321
Ni	22.42	0.049	0.9818	17.62	20.23	1.664	0.6094	0.9763

Table 10. Calculated separation factor (SF) for biosorption of Pb^{2+} Cu^{2+} Zn^{2+} and Ni^{2+} on *Mangifera sp.* biomass.

Ci	SF of Pb	SF of Cu	SF of Zn	SF of Ni
25	0.27027	0.396432	0.4111	0.449438
50	0.15625	0.247219	0.258732	0.289855
75	0.10989	0.179614	0.188768	0.213904
100	0.084746	0.141044	0.148588	0.169492
125	0.068966	0.11611	0.122511	0.140351
150	0.05814	0.098668	0.104221	0.11976

reveals the biosorption of Ni^{2+} by *Mangifera* sp. biomass as a function of initial concentration of control flasks or blank solutions. Uptake capacity increases to 17.618 mgg-1 and removal of Ni^{2+} from solution is more at low initial concentration that is, maximum 82.299% at 24.01 mgL-1 concentration. The same trend is observed as in the previous three metals but with a slight reduction in both parameters. The Langmuir and Freundlich isotherms parameters of Ni^{2+} biosorption by *Mangifera* sp. biomass and plots are shown in Table 8 while Figure 4 indicates that both models well describe the experimental data as the values of coefficient of determination are 0.9818 and 0.9763 for Langmiure and Freundlich isotherms, respect-tively, which is very close to 1.

The data in Table 10 shows that, the sorption of metals on *Mangifera* sp. biomass increase as the initial metal ion concentration increases from 25 to 150 mgl^{-1}, indicating that biosorption is even favorable for the higher initial metal ion concentrations (Figure 5). The biosorption process is favorable for metal removal at all concentrations investigated. According to this classification, removal ability tends to be in the order Pb > Cu >Zn > Ni.

Previous order illustrates that, initially, equilibrium for metals uptake is more favorable for *Mangifera* sp., its sorption capacity and selectivity is the same as presented in Table 9. The trend presented by SF in Figure 5 also provides information that the *Mangifera sp.* biomass is a more effective and excellent adsorbent for metal at lower metal concentrations.

Surface coverage (θ)

To account for absorption behavior of the metal ions on the biomass, the Langmuir type equation related to surface coverage is used. The equation is expressed as follow

$$bC_i = \theta/(1-\theta) \text{ and } \theta = bCi/(1+bC_i)$$

Where, b is the absorption coefficient, Ci the initial con-

Table 11. Surface coverage (*θ*) of lead, copper, zinc and nickel for *Mangifera sp.* biomass.

Ci (mgL^{-1})	θ of Pb	θ of Cu	θ of Zn	θ of Ni
25	0.737469	0.603664	0.568682	0.540545
50	0.83849	0.760253	0.737651	0.703189
75	0.891805	0.814024	0.815853	0.782262
100	0.916934	0.860762	0.854156	0.832195
125	0.929533	0.882342	0.878461	0.858814
150	0.940899	0.899453	0.895411	0.879112

Table 12a. Uptake capacity of *Mangifera sp.*and percentage removal of lead in BMS.

Ci	(Pb Cu) Binary sol.		(Pb Ni) Binary sol.		(Pb Zn) Binary sol.	
	q	% removal	q	% removal	q	% removal
26.01	4.386	84.31373	4.624	90.3125	3.834	75.92079
48.07	7.884	82.00541	8.27	84.38776	7.76	78.46309
76.32	12.358	80.96174	12.464	82.16216	11.654	77.90107
102.21	17.3	84.62968	17.278	85.45005	15.536	78.15676
122.14	19.596	80.21942	19.998	81.19367	19.068	76.57831
147.41	24	81.4056	23.958	80.2882	19.296	64.79952

Table 12b. Uptake capacity of *Mangifera sp.*and percentage removal of lead in SMS.

Ci	q	% Removal
26.01	4.786	92.00308
48.07	8.284	86.16601
76.32	12.758	83.58229
102.21	17.7	86.58644
122.14	19.996	81.85689
147.41	24.4	82.76236

centration and θ the surface coverage.

The fraction of biomass surface covered by metal ion was studied by plotting the surface coverage values (θ) against metal ions concentration. The data is presented in Table 11 and Figure 7. The figure shows that, increase in initial metal ion concentration for *Mangifera* sp. biomass increases the surface coverage on the biomass until the surface is nearly fully covered with a monomolecular layer. Further examination of Figure 7 reveals that the surface coverage ceases to vary significantly with concentration of metal ions at higher levels. Surface coverage value for metal ions on absorbents of *Mangifera* sp is in the following order Pb > Cu > Zn > Ni.

Surface coverage value indicated that *Mangifera* sp. is the most effective in uptake of Pb^{2+} and then other metal ions from aqueous solutions at all initial concentrations are evaluated in study.

BMS batch sorption study profile

In the BMS, one metal ions is used as the main metal, the initial concentration of which was varied to determine the maximum amount absorbed in the presence of fixed concentration of co-ions.

Comparing the intercationic effect in BMS biosorption of Pb by *Mangfera* sp. biomass in Tables 12a and b and Figure 8, the inhibition of Pb^{2+} sorption in the presence of $Cu2^{+}$, Ni^{2+} and Zn^{2+} co-ions is observed. The sorption of Pb reduces in the presence of Cu^{2+} and Ni^{2+} from 24.4 to 24 and 23.95 mgg^{-1}, respectively, compared to its sorption from SMS. There is no much significant change. In the case of Zn^{2+} co-ion, the uptake capacity of biososrbent reduces to 19.296 mgg^{-1}. This reduction in sorption or uptake capacity (q) is observed at highest concentration of lead in solution. The percentage removal of lead is observed in all binary metal system of lead as compared

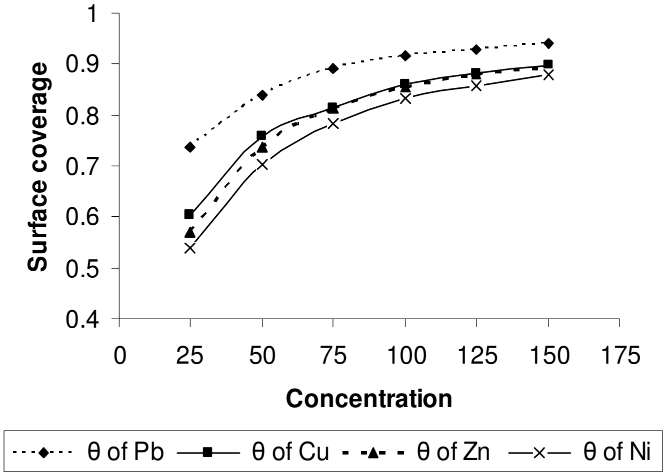
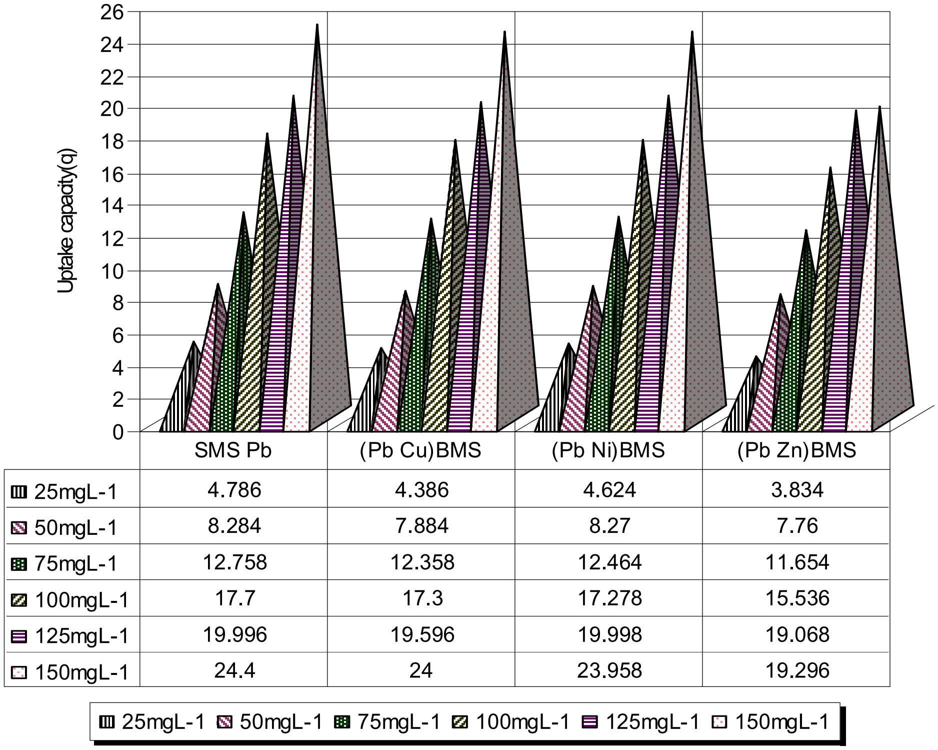


Figure 7. A plot of surface coverage (*θ*) against concentration of lead, copper, zinc and nickel for *Mangifera* sp. biomass.



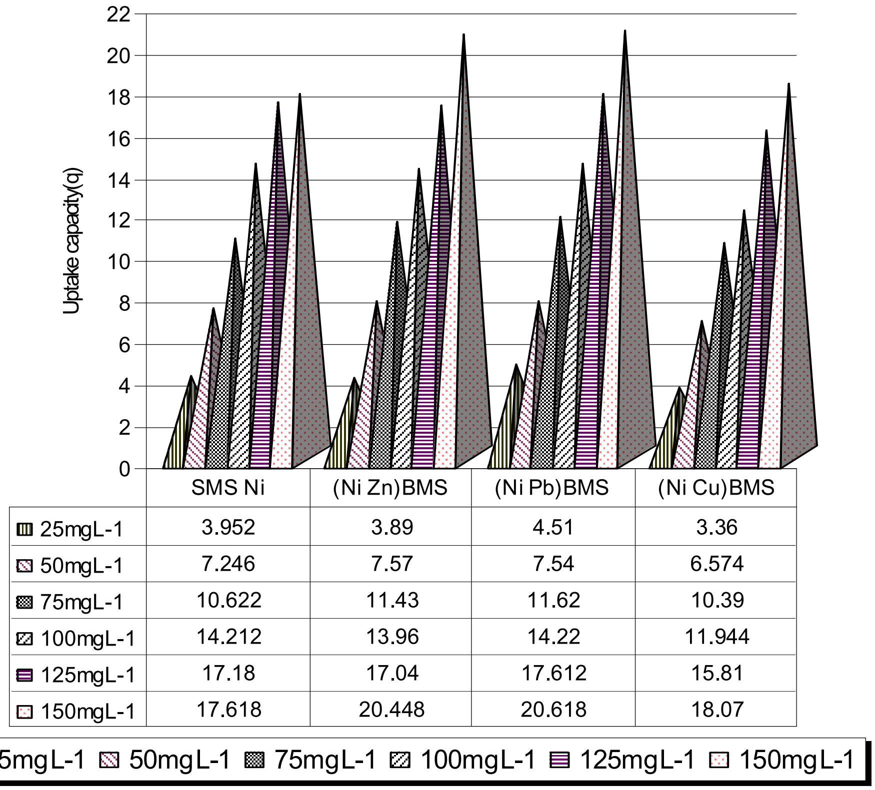
	SMS Pb	(Pb Cu)BMS	(Pb Ni)BMS	(Pb Zn)BMS
▥ 25mgL-1	4.786	4.386	4.624	3.834
▧ 50mgL-1	8.284	7.884	8.27	7.76
▦ 75mgL-1	12.758	12.358	12.464	11.654
▨ 100mgL-1	17.7	17.3	17.278	15.536
▤ 125mgL-1	19.996	19.596	19.998	19.068
□ 150mgL-1	24.4	24	23.958	19.296

Figure 8. Comparison of uptake capacity (q) of Pb^{2+} in SMS and BMS by *Mangifera* sp.

to percentage removal in single metal system.

Interestingly, Ni^{2+} sorption increases in the presence of co-ions Cu^{2+}, Pb^{2+} and Zn^{2+} as compared to its sorption in SMS (Tables 13a and b). Uptake capacity of *Mangifera* sp. biosorbent for Ni^{2+} increases from 17.618 in SMS to 20.448 and 20.176 mgg^{-1} in the presence of Zn^{2+} and Pb^{2+} co-ions and a slight increase in the presence of Cu^{2+}, that is, 18.07 mgg^{-1} (Figure 9).

The effect of Ni^{2+}, Pb^{2+} and Zn^{2+} on the uptake of copper by *Mangifera* sp. biosorbent is observed as Cu^{2+} sorption is inhibited by the presence of co-ion compared to its sorption from SMS and the amount of metal ions sorbed is less as compared to sorbed from Cu^{2+} solution of SMS (Tables 14a and b). The data in reveal that uptake capacity of Cu^{2+} is 29.378 mgg^{-1} in SMS but it reduces to 23.662, 23.192 and19.208 mgg^{-1} in the presence of Zn^{2+},



	SMS Ni	(Ni Zn)BMS	(Ni Pb)BMS	(Ni Cu)BMS
25mgL-1	3.952	3.89	4.51	3.36
50mgL-1	7.246	7.57	7.54	6.574
75mgL-1	10.622	11.43	11.62	10.39
100mgL-1	14.212	13.96	14.22	11.944
125mgL-1	17.18	17.04	17.612	15.81
150mgL-1	17.618	20.448	20.618	18.07

Figure 9. Comparison of uptake capacity (q) of Ni^{2+}in SMS and BMS by *Mangifera* sp.

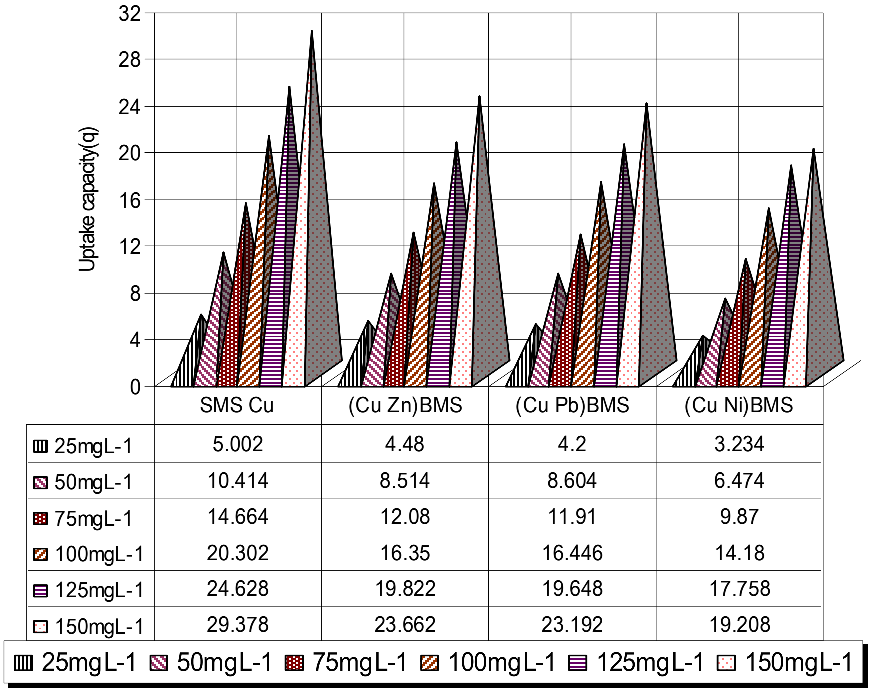
Table 13a. Uptake capacity of *Mangifera sp.*and percentage removal of nickel in BMS.

	(Ni Zn) Binary sol.		(Ni Pb) Binary sol.		(Ni Cu) Binary sol.	
Ci	**q**	**% removal**	**q**	**% removal**	**q**	**% removal**
24.1	3.89	79.87013	4.51	86.0687	3.36	66.01179
48.85	7.57	77.8002	7.54	76.47059	6.574	67.60592
74.2	11.43	77.654	11.62	76.34691	10.39	68.0865
99.95	13.96	70.14851	14.22	70.43091	11.944	59.74987
124.44	17.04	68.14935	17.612	69.72288	15.81	63.49398
149.24	20.448	68.29466	20.618	68.06867	18.07	59.97345

Table 13b. Uptake capacity of *Mangifera sp.*and percentage removal of nickel in SMS.

Ci	q	% Removal
24.01	3.952	82.29904
48.35	7.246	74.93278
73.32	10.622	72.4359
101.21	14.212	70.21045
124.14	17.18	69.19607
148.41	17.618	59.35584

Pb^{2+} and Ni^{2+},respectively. The reduction is significant in (Cu, Ni) binary solution (Figure 10). Zn^{2+} uptake is not affected significantly in the presence of Cu^{2+} and Ni^{2+} co-ions in BMS and Pb^{2+} show significant effect on Zn^{2+} sorption. Zn^{2+} sorption reduces from 18.932 to 15.09 mgg^{-1} in the presence of $Pb2^{+}$ as compared to



	SMS Cu	(Cu Zn)BMS	(Cu Pb)BMS	(Cu Ni)BMS
25mgL-1	5.002	4.48	4.2	3.234
50mgL-1	10.414	8.514	8.604	6.474
75mgL-1	14.664	12.08	11.91	9.87
100mgL-1	20.302	16.35	16.446	14.18
125mgL-1	24.628	19.822	19.648	17.758
150mgL-1	29.378	23.662	23.192	19.208

Figure 10. Comparison of uptake capacity (q) of Cu^{2+}in SMS and BMS by *Mangifera* sp.

Table 14a. Uptake capacity of *Mangifera sp.*and percentage removal of copper in BMS.

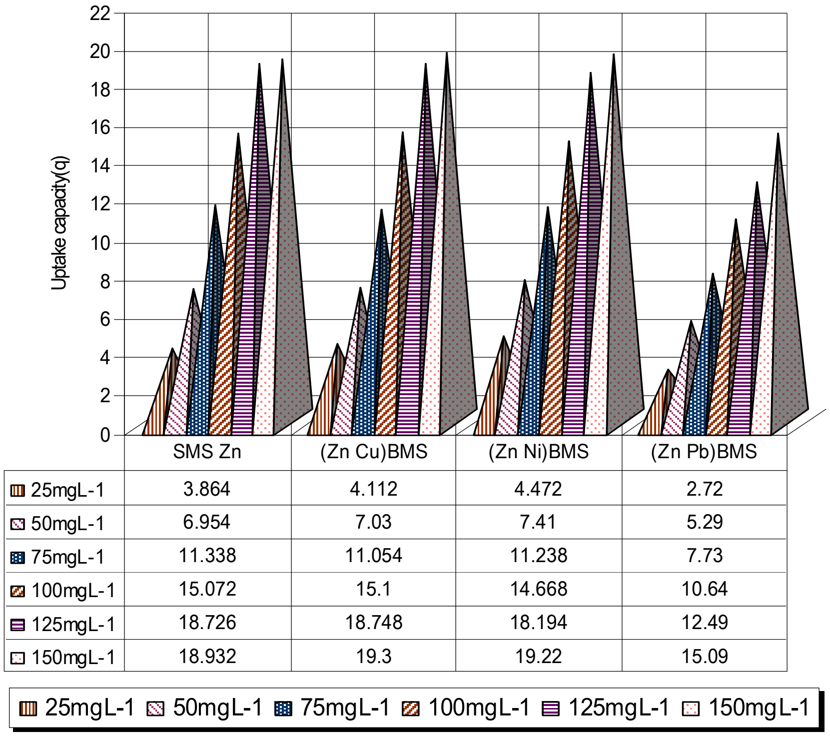
Ci	**(Cu Zn) Binary sol.**		**(Cu Pb) Binary sol.**		**(Cu Ni) Binary sol.**	
	q	**% removal**	**q**	**% removal**	**q**	**% removal**
24.65	4.48	87.32943	4.2	85.1927	3.234	66.21622
51.87	8.514	83.6839	8.604	82.93811	6.474	63.63279
73.9	12.08	80.96515	11.91	80.58187	9.87	65.8439
102.05	16.35	80.90054	16.446	80.57815	14.18	70.02469
124.14	19.822	80.21204	19.648	79.13646	17.758	70.66454
147	23.662	79.74521	23.192	78.88435	19.208	64.66469

Table 14b. Uptake capacity of *Mangifera* sp.and percentage removal of copper in SMS.

Ci	**q**	**% Removal**
25.01	5.002	86.84526
52.07	10.414	76.37795
73.32	14.664	76.52755
101.51	20.302	80.00197
123.14	24.628	80.26636
146.89	29.378	76.60835

sorption by *Mangifera* sp. biomass in SMS. This is shown in Tables 15a and b and Figure 11.

The summary of intercationic effect phenomenon on absorption by *mangifera* sp. is as follows:



	SMS Zn	(Zn Cu)BMS	(Zn Ni)BMS	(Zn Pb)BMS
▥ 25mgL-1	3.864	4.112	4.472	2.72
▨ 50mgL-1	6.954	7.03	7.41	5.29
▦ 75mgL-1	11.338	11.054	11.238	7.73
▨ 100mgL-1	15.072	15.1	14.668	10.64
▤ 125mgL-1	18.726	18.748	18.194	12.49
☐ 150mgL-1	18.932	19.3	19.22	15.09

Figure 11. Comparison of uptake capacity (q) of Zn^{2+}in SMS and BMS by *Mangifera* sp.

Table 15a. Uptake capacity of *Mangifera sp.*and percentage removal of zinc in BMS.

Ci	(Zn Cu) Binary sol.		(Zn Ni) Binary sol.		(Zn Pb) Binary sol.	
	q	% removal	q	% removal	q	% removal
24.3	4.112	84.78351	4.472	84.85769	2.72	56.00823
48.75	7.03	71.0819	7.41	71.94175	5.29	54.25641
76	11.054	72.8195	11.238	72.73786	7.73	50.84211
99.08	15.1	73.76649	14.668	72.68583	10.64	53.6738
124.09	18.748	74.2495	18.194	72.3017	12.49	50.31832
148.45	19.3	63.80165	19.22	63.49521	15.09	50.08297

Table 15b. Uptake capacity of *Mangifera sp.*and percentage removal of zinc in SMS.

Ci	q	% Removal
23.01	3.864	83.96349
49.07	6.954	70.85796
77.32	11.338	73.31868
102.21	15.072	73.73055
126.14	18.726	74.22705
149.41	18.932	63.35587

1. Zn^{2+} presence significantly affects Pb^{2+} sorption and vice versa.

2. Cu^{2+} presence significantly affects Ni^{2+} sorption and vice versa.

CONCLUSION

The following conclusions can be drawn from the present study:

1. The harvesting of the *Mangifera* sp. biomass is a relatively simple procedure, and can be obtained without excessive cost.
2. The adsorption range of metal ions includes Pb^{2+}, $Cu2^{+}$, Ni^{2+} and $zinc^{2+}$ ions from dilute acidic solutions of pH 4 – 6.
3. The non-living biomass of *Mangifera* sp. present comparable biosorption capacity for Pb^{2+}, Cu^{2+}, Zn^{2+} and Ni^{2+} ions with other types (sources) of biosorbent materials found in previous literature.
4. Efficiency of the biomass indicates that it is effective to remove metal ions from single metal solutions as well as in the presence of other co-ions with the main metal of solution.

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