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Intercationic effect on biosorbent efficacy

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ABSTRACT

The efficacy of the biosorbent coconut hust (*Cocos nucifera*) was tested for the removal of lead, copper, zinc, and nickel metal ions using batch experiments in multimetal solution system under controlled experimental conditions. It is found that metal sorption increases when the equilibrium metal concentration rises. At highest experimental solution concentration (150 mg/L), the removal of metal ions was 92.52% for lead, 79.55% for copper, 63.23% for zinc, and 68.10% for nickel, while at lowest experimental solution concentration (25 mg/L), the removal of metal ions was 94.80% for lead, 86.81% for copper, 84.63% for zinc, and 82.36% for nickel. Biosorption equilibrium isotherms were plotted for metal uptake capacity (q) against residual metal concentrations (C_f) in solution. The q vs. C_f sorption isotherm relationship was mathematically expressed by Langmuir and Freundlich models. The values of separation factor were between zero and one indicating favorable sorption for four tested metals on the biosorbent. The surface coverage values were approaching unity with increasing solution concentration, indicating effectiveness of the biosorbent.

Keywords: Coconut husk; Biosorbent; Multimetal system; Langmuir and freundlich models; Surface coverage; Separation factor; Efficacy

1. Introduction

The pollution of water resources due to the disposal of heavy metal contaminated effluents has been an increasing worldwide concern for the last few decades. Heavy metal pollution is spreading throughout the world with the expansion of industrial activities; lead, nickel, zinc, and copper are known to be commonly used heavy metals. Many industries, especially plating and battery, release heavy metals like nickel and copper in wastewaters. Sources of heavy metal contaminants in soils include metalliferous mining and smelting, metallurgical industries, sewage sludge treatment, warfare and military training, waste disposal sites, agricultural fertilizers, and electronic industries [1].

These metals, which find many useful applications in our life, are very harmful if they are discharged or may discharge into natural water resources and may

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pose a serious health hazard. The heavy metals have high mobility in aquatic systems and in general may produce high toxicity [2]. Due to nonbiodegradability, metal ions accumulate and their amounts are increased along the food chain. Hence, their toxic effects are more pronounced in the animals at higher trophic levels. The different methods are used for the removal of heavy metals as important contaminants in the water and wastewater.

In chemical methods, effective decrease in heavy metals to acceptable levels requires excess of chemicals that increase the costs because of generating the voluminous sludge [3]. Phytoremediation is the use of certain plants to clean up soil, sediment, and water contaminated with metals. 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 it imperative for a cost-effective treatment method that is capable of removing heavy metals from aqueous effluents [4].

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 physicochemical process. The biosorption process involves a solid phase (sorbent or biosorbent; biological material) and a liquid phase (solvent, normally water) containing dissolved species to be sorbed (sorbate, metal ions) due to high affinity of biosorbent for the sorbate species, the later is attracted and bound there by different mechanisms [5].

Different mechanisms involved in biosorption can operate simultaneously to varying degrees [6]. Temperature seems not to influence the biosorption performances in the range of 20–35˚C [7]. pH seems to be the most important parameter in the biosorptive process. It affects the solution chemistry of the metals, the activity of the functional groups in the biomass and the competition of metallic ions [8]. Biomass concentration in solution seems to influence the specific uptake. For lower values of biomass concentrations, there is an increase in the specific uptake [9]. Metal affinity to the biomass can be manipulated by pretreating the biomass with alkalies, acids, detergents, and heat, which may enhance the amount of the metal sorbed. When nonviable biomass is used in the removal of heavy metals, alkali pre-treatment is an effective method to improve the biosorption capacity for metal ions [10]. Hence, the biosorption efficiency of dead biomass may be greater, equivalent to, or less than that of live biomass depending on the pretreatment method applied [11]. It is necessary to carry out more detailed studies to understand why enhancement or reduction in adsorption capacity occurs under specific pretreatment conditions.

Previous studies on metal biosorption have been restricted to simple solution of only one metal. Biomass, which 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 has been exploited only a limited extent. The removal of lead (Pb) form and found that Pb has highest sorption properties in aqueous solution by adsorption on nonliving *Penicillium chrysogenum* biomass as compared to other selected metals and also observed that the sorption up take of Pb remained unchanged in the presence of Zn and increased in the presence of Cd [12]. Biosorption process was studied in rice husk in aqueous solution and found that rice husk (RH) ash was a good adsorbent [13]. Similarly, brown marine algae, *Ecklonia radiata*, has been used for the development of an efficient biosorbent material for heavy metal removal from wastewater [14], while the biosorption of Zn by six fungi species (*Rhizopus arrhizus*, *Mucor recemosus*, *Mycotypha aficana*, *Aspergillus nidulans*, *Aspargillus nigar*, and *Schizosocharomyces pomb*) were also studies and found that biosorption generally decreased with an increase in biosorbent particle size and its concentration [15]. Similarly, biowastes of fruit juice industry used as biosorbent for the removal of six toxic heavy metals, such as Hg (II), Pb (II), Cd (II), Cu (II), Zn (II), and Ni (II), from aqueous solution were studied and found an efficient removal at low pH in aqueous solution [16]. Chandra et al. (1994) used the bark of *Hemidesmus indicus* commonly called as *Indian sarsaparilla* as biosorbent for the removal of lead from aqueous streams [17]. This was an attempt to remove lead from the lead-contaminated waters (both ground and surface) from industrially contaminated sites. Saeed et al. [18] used the milling agro waste of *Cicer arientinum* (chickpea var. black gram) as biosorbent for the removal of heavy metal ions efficiently from aqueous solutions with the selectivity order of $Pb > Cd > Zn > Cu > Ni$ [18]. Bulut and Baysal [19] investigated the adsorption of Pb (II) ions from aqueous solutions on wheat bran (WB) as a function of initial concentration, adsorbent dose, adsorbent particle size, agitation speed, temperature, contact time, and pH of solution, while King et al. [20] studied the biosorption of lead ions from aqueous solution by *Syzygium cumini* L. in a batch adsorption system as a function of pH, contact time, lead ion concentration, adsorbent concentration, and adsorbent size. Hameed et al. [21] studied the sorption of basic dye from aqueous solutions by banana stalk waste (BSW), an abundant agricultural waste in Malaysia, was in a batch system with respect to pH and initial dye concentration. Wan Ngah and Hanafiah [22] investigated the efficiency of sodium hydroxide treated rubber (*Hevea brasiliensis*) leaves powder (NHBL) for removing copper ions from aqueous solutions. Ucun et al. [23] investigated the biosorption properties of copper (II) and zinc (II) onto a cone biomass of *Pinus sylvestris* L. using batch techniques. The removal of chromium (VI) from aqueous solution by walnut hull (a local low-cost adsorbent) was also studied. When compared with the various other adsorbents reported in the literature, the walnut hull in this study shows very good promise for practical applicability [24].

The objective of this study is to develop an inexpensive and effective biosorbent that is easily available in large quantities and economically feasible for multiple metal ions in solution. Coconut husk (*Cocos nucifera*) is tested during this study for the biosorption of multiple metal ions in multimetal system.

2. Methodology

2.1. Preparation of biosorbent

Coconut husk (*C. nucifera*) was collected from local market of the city. The biomass was dried in 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˚C and ground to powder with kitchen grinder of Moulinex. Grinded biomass was further thoroughly washed with distilled water till the color of washing water clear. The powdered biomass was dried in oven at 50˚C until a constant weight is attained after drying.

2.2. Grinding and sieving of biosorbent

The biosorbent was again ground to powder and was sieved for grading of size. Three suitable mesh sizes were chosen.

The particles of four sizes separated out

(1) particle size of less than 255 μm
(2) particle size from 255 to 355 μm
(3) particle size from 355 to 500 μm
(4) particle size of greater than 500–710 μm

The aforesaid particle size No. 2 was selected for further study, because the amount of No. 1 size was too less and No.3 and No.4 sizes will show less efficiency because of less surface area as compared to No. 2 size.

2.3. Stock solutions of metal ions

About 1,000 mg L^{-1} stock solutions were prepared by dissolving dried salts 1.598 g of Pb $(NO_3)_2$, 3.929 g of $CuSO_4{\cdot}5H_2O$, 3.107 g of $NiSO_4{\cdot}6H_2O$, and 4.549 g of $Zn(NO_3)_2{\cdot}6H_2O$ in the double distilled water (DDW) and diluting quantitatively up to the 1,000 ml using DDW. The resulting stock solutions were stored in the airtight plastic bottle.

2.4. Intermediate solutions

Intermediate solutions of different concentrations for experimental purpose were prepared from stock solutions in DDW applying the dilution formula.

$$C_1V_1 = C_2V_2 \tag{1}$$

2.5. Batch biosorption studies of multimetal system

In all sets of experiments, fixed volume of single metal ion solutions (100 ml) of varying 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 255–355 μ at 30°C and 100 round/min shaking speed for 12 h. Twelve hours of equilibrium period for sorption experiment were used to ensure equilibrium. Previous studies indicated that equilibrium was reached in much less time than this, for example, 80 min Cu on sour orange residue [25], 3 h for Ni–Pb binary metal system (BMS) by *Phanerochaete chrysosporium* [26]. 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 flasks were removed, and the solution was separated from the biomass by filtration through filter paper (Whatman No. 40 ashless). Binary metal solutions were tested under same experimental conditions. In the binary and multimetal system, one metal ion was used as the main metal, the initial concentration of which was varied to determine the maximum amount sorbed in the presence of fixed initial concentration of a co-ions.

2.6. 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 experiment 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 sorbed. The metal ions contents in all the samples were determined by flame atomic absorption spectrometry using a Perkin Elmer AAS (A. Analyst 300).

2.7. Calculation of metal uptake (sorption capacity)

The quality of sorbent material is judged according to how much sorbate it can att'ract and retain in an immobilized form. For this, it is customary to determine the metal uptake (sorption capacity), q, by the biosorbent as the amount of sorbate bound by the unit of solid phase.

Amount of metal bound by the sorbent which disappeared from the solution was calculated based on the mass balance for the sorbent in the system.

$$q = \frac{V(C_\mathrm{i} - C_\mathrm{f})}{S} \tag{2}$$

q, metal ion uptake capacity (mg g^{-1}); C_i, initial concentration of metal in solution, before the sorption analysis (mg L^{-1}); C_f, final concentration of metal in solution, after the sorption analysis (mg L^{-1}); S, dry weight of biosorbent (g); and 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.

2.8. Freundlich and Langmuir model

To characterize the biosorption for single metal component system, Langmuir and Freundlich models are 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 [27]

$$q = \frac{q_\mathrm{max} b C_\mathrm{f}}{(1 + bC_\mathrm{f})} \tag{3}$$

It is linearized to the form

$$1/q = 1/q_\mathrm{max} + 1/(b \cdot q_\mathrm{max})(C_\mathrm{f}) \tag{4}$$

where q_max and b are the Langmuir constants.

The Freundlich equation of adsorption isotherm is [27]

$$q = K(C_\mathrm{f})_1^{/n} \tag{5}$$

Its linearized form is represented by the equation

$$\log q = \log K + (1/n)\log C_\mathrm{f} \tag{6}$$

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

2.9. Separation factor

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 Langmuir isotherm was expressed in terms of dimensionless constant called the separation factor. It is defined by the following relationship.

$$Sf = 1/(1 + bC_i) \tag{7}$$

2.10. 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 follows:

$$\begin{aligned} & bC_i = \theta/(1-\theta) \\ \text{and} \quad & \theta = bC_i/(1 + bC_i) \end{aligned} \tag{8}$$

3. Results

Efficiency of the non conventional biosorbent of plant origin is tested for the removal of metal ions such as Pb^{2+} Cu^{2+} Ni^{2+}, and Zn^{2+} from synthetic solutions in single and binary metal solutions. The objective is to develop inexpensive and effective metal ions sorbent that is available easily in large quantity and feasible economically. Biosorbent, coconut husk (*C. nucifera*), is tested for efficacy in single metal system (SMS) and intercationic effect in BMS on biosorption efficiency.

3.1. Single metal system batch sorption study profile

Data in Table 1 reveals the biosorption of Pb^{2+} Cu^{2+} Ni^{2+}, and Zn^{2+} by *C. nucifera* biomass as a function of initial concentration of control flasks or blank solutions. The same trend of uptake capacity along with percentage removal is observed in all four analyzed metal ions with the slight reduction in both parameters. The removal of metal ions from solution is more at low initial concentration that is maximum 92.003% at 26.01 mg L^{-1} for Pb^{2+}, 88.845% at 25.01 mg L^{-1} for Cu^{2+}, 82.299% at 24.01 mg L^{-1} for Ni^{2+}

Table 1
Effect of metal ion concentration percentage removal and uptake capacity in SMS

Element	Concentration (mg L^{-1})	C_i (mg L^{-1})	C_f (mg L^{-1})	Removal (%)
Pb^{2+}	25	26.01	2.08	92.00
	50	48.07	6.65	86.16
	75	76.32	12.53	83.58
	100	102.21	13.71	86.58
	125	122.14	22.16	81.85
	150	147.41	25.41	82.76
Cu^{2+}	25	25.01	3.29	86.84
	50	52.07	12.3	76.37
	75	73.32	17.21	76.52
	100	101.51	20.3	80.00
	125	123.14	24.3	80.26
	150	146.89	34.36	76.60
Zn^{2+}	25	23.01	3.69	83.96
	50	49.07	14.3	70.85
	75	77.32	20.63	73.31
	100	102.21	26.85	73.73
	125	126.14	32.51	74.22
	150	149.41	54.75	63.35
Ni^{2+}	25	24.01	4.25	82.29
	50	48.35	12.12	74.93
	75	73.32	20.21	72.43
	100	101.21	30.15	70.21
	125	124.14	38.24	69.19
	150	148.41	60.32	59.35

and 83.963% at 23.01 mgL^{-1} for Zn^{2+} concentration. Table 2 shows the Langmuir and Freundlich isotherms parameters of Pb^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}biosorption by *Mangifera sp*. biomass and plots in Figs. 1 and 2 indicate that both models adequately fit the experimental data in all cases, being the coefficients of determination in the range of 0.9256–0.9818 for Langmuir isotherms and 0.9306–0.9763 for Freundlich isotherms which is very close to 1.

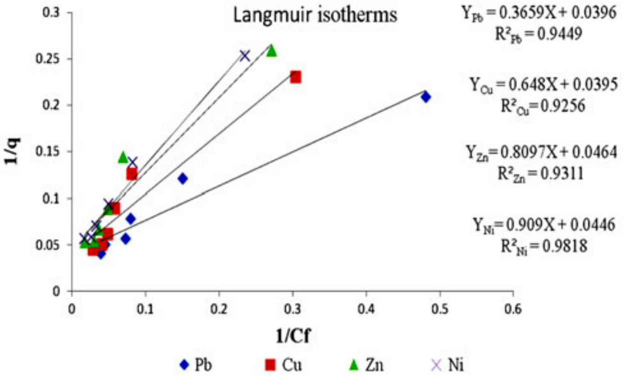


Fig. 1. Langmuir adsorption isotherm for Pb^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}.

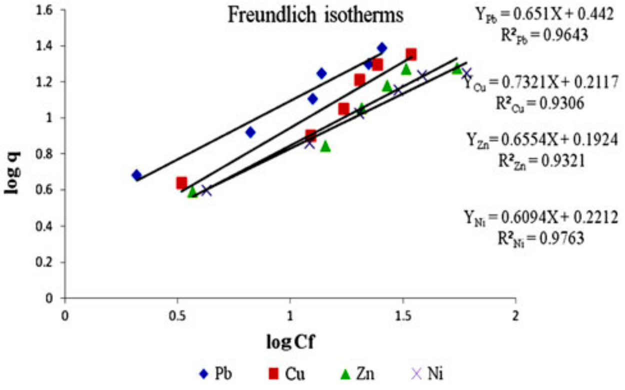


Fig. 2. Freundlich adsorption isotherm for Pb^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}.

3.2. *Binary metal system batch sorption study profile*

In the BMS, one metal ion is used as the main metal, the initial concentration of which was varied to determine the maximum amount sorbed in the presence of fixed concentration of a co-ions. The other conditions are as follows

Table 2
Comprison of Langmuire and Freundlich isotherm for metals

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

- particle size between 255 and 355 µm,
- at 30 ± 1°C and 100 round/min shaking speed for 12 h,
- 0.5 g biosorbent amount,
- pH range 4–6.

In all sets of experiments, 100 ml volume of BMS solutions with varying concentrations (25, 50, 75, 100, 125, and 150 mg L^{-1}) of main metal and 25 mg L^{-1} of affecting metal concentration or co-ion in the same solution in conical flasks of Pyrex made of 100–200 ml working volume was thoroughly mixed with biosorbent dose of 0.5 g and size 255–355 µm at 30 ± 1°C and 100 round/min 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 (Whatman No.40 ashless). After analysis following results obtained are presented in tabulated form. The uptake capacity (q in mgg^{-1}) of biosorbent and percentage of metal removed from solution is calculated. These results are compared with the efficacy of biosobent with SMS.

Comparing the intercationic effect in BMS biosorption of Pb by the biomass in Fig. 7, it is observed the inhibition of Pb^{2+} sorption in the presence of Cu2^{+}, Ni^{2+}, and Zn^{2+} co-ions. The sorption of Pb reduces in the presence of Cu^{2+} and Ni^{2+} from 24.4 to 24 and 23.95 mg g^{-1}, respectively, compared with its sorption from SMS. It is not much significant change. In case of Zn^{2+} co-ion, the uptake capacity of biososrbent reduces to 19.296 mg g^{-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 BMS of lead as compared 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 as shown in Fig. 8. Uptake capacity of the biosorbent for Ni^{2+} increases from 17.618 in SMS to 20.448 and 20.176 mg g^{-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 mg g^{-1}.

The effect of Ni^{2+}, Pb^{2+}, and Zn^{2+} on the uptake of copper by the biosorbent is observed as:

- Cu^{2+} sorption is inhibited by the presence of co-ion compared with its sorption from SMS and the amount of metal ions sorbed is less as compared to sorbed from Cu^{2+} solution of SMS.
- The results in Fig. 9 reveal that uptake capacity of Cu^{2+} is 29.378 mg g^{-1} in SMS, but it reduces to 23.662, 23.192, and 19.208 mg g^{-1} in the presence of Zn^{2+}, Pb^{2+}, and Ni^{2+}, respectively. The reduction is significant in (Cu, Ni) binary solution.
- Zn^{2+} uptake is not effected significantly in the presence of Cu^{2+} an 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 mg g^{-1} in the presence of Pb2^{+} as compared to sorption by both biosorbent in SMS. This is shown in Fig. 10.

The summary of intercationic effect phenomenon on sorption is under

(1) Zn^{2+} presence significantly affect Pb^{2+} sorption and vice versa.
(2) Cu^{2+} presence significantly affect Ni^{2+} sorption and vice versa.

4. Discussion

The rate of adsorption 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 Fig. 3 and Fig. 4 in general, the data reveal that sorption capacity of sorbent augment with increase in initial concentration of metal ions. This sorption characteristic represent that surface saturation was dependent on the initial metal ion concentrations. At low-concentration adsorption 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 [28].

It is found that as metal ion concentration is reduced, the metal ion biosorption rate reached to high; however, when the metal ion concentration is high, the metal removal rate decreased. Such decline in percentage removal rate is probably caused by the

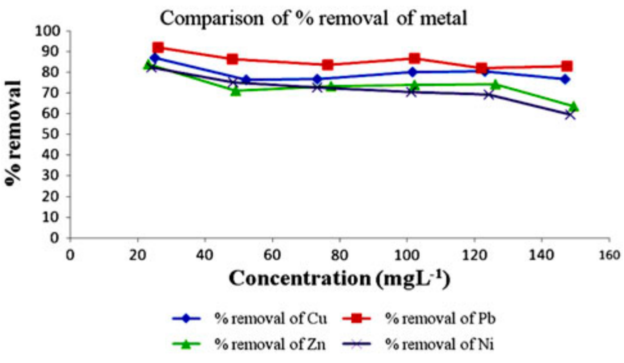


Fig. 3. Comparison of percentage removal as a function of metal ions concentration.

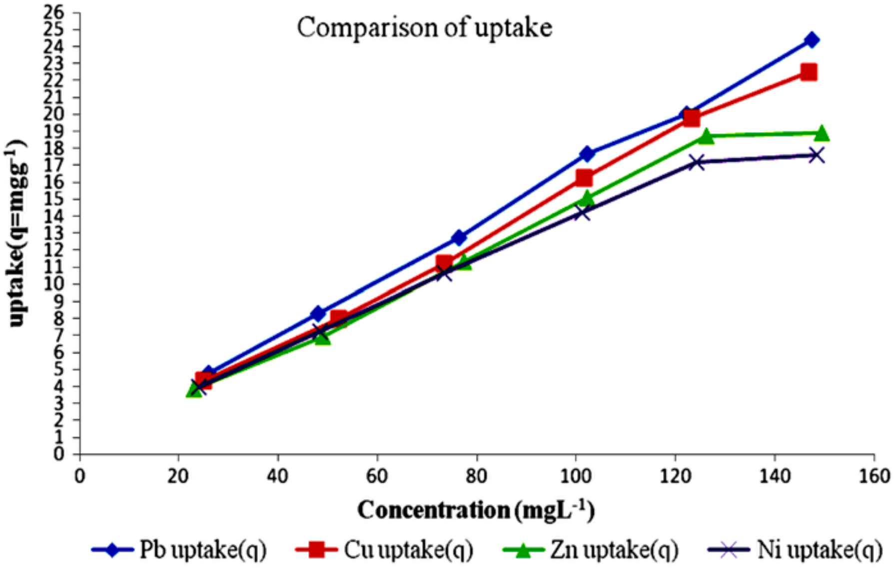


Fig. 4. Comparison of uptake capacity (mgg^{-1}) and percentage removal as a function of metal ions concentration by *C. nucifera* biosorbent.

saturation of some adsorption sites. The results are in agreement with Chen and Wang (2007) [29].

The selectivity order for metal ions toward the studied biomass is

Pb >Cu >Zn >Ni

This order is same as searched by Zhang (2005) [30] and comparable with Saeed et al. (2005) [18]. This differential sorption of metal ions may be ascribed to the difference in their ionic radii. The smaller the ionic radius, the greater the tendency to hydrolyze, leading to reduced sorption. The ionic radii of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} are 1.19 Å, 0.73 Å, 0.74 Å, and 0.67 Å, respectively. The results are in similar to previous study by Horsefall and Spiff [28] and Hanif et al. [31].

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

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

$$1/q = 1/q_{max} + 1/(bq_{max})(C_f) \tag{9}$$

Constant b that is related to the energy of adsorption through the Arrhenius equation. The higher the constant b, the higher is the affinity of the sorbent for the sorbate. $q_{\max}$ 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 sorbate at the concentration C_f [27].

According to the above data, the affinity orders of *M. Sp.* biosorbent is

Pb >Cu >Zn >Ni

Langmuir isotherm, which represents that monolayer of sorbate, is formed on biosorbent.

Adsorption–partition constants are determined for metals using the following log form of the Freundlich isotherm

$$\log q = \log K + (1/n)\log C_f \tag{10}$$

where q is the metal ion sorbed (mg g^{-1}), C_f the equilibrium concentration of metal ion solution in mg L^{-1}, K and n are Freundlich constants. The constants K and $1/n$ were determined by linear regression from the plot of log q against $\log C_f$. K is a measure of the degree or strength of adsorption. Small value of K indicate the minimal sorption and large value indicates the more sorption [28], while $1/n$ is used as an indication of whether adsorption remains constant (at $1/n = 1$) or decreases with increasing adsorbate concentrations (with $1/n \neq 1$). The $q_{\max}$ value is the maximum value of q and is important to identify the biosorbent for highest metal uptake capacity and as such useful in scale-up considerations [31]. The magnitude of the experimental $q_{\max}$ for *M. sp.* biomass is found to 24.40, 22.51, 18.93, and 17.62 mg g^{-1} for all the four, that is, lead, copper zinc, and nickel metal ions are comparable with theoretically calculated $q_{\max}$ values from Langmuir and Freundlich isotherm models presented in Table 2. The maximum sorption capacity is observed of lead on *C. nucifera* suggesting that it is a potential biosorbent for the removal of lead as well as the other three tested metals.

4.1. Separation Factor (SF)

The shape of the Langmuir isotherm can be used to predict whether a sorption 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

$$SF = 1/(1 + bCi) \tag{11}$$

where SF is the dimensionless equilibrium parameter or separation factor, *b*, the constant from Langmuir equation and Ci the initial metal ion concentration of 100 mg L^{-1}. The parameter, SF, indicates the shape of the isotherm and nature of the sorption process [32]. SF value between 0 and 1 represents favorable isotherm. The SF values of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} for *C. nucifera* biomass is calculated from above equation and plotted against initial metal ion concentration [31].

The data in Table 3 show that, the sorption of metals on *C. nucifera* biomass increase as the initial metal ion concentration increase from 25 to 150 mg L^{-1}, indicating that adsorption is even favorable for the higher initial metal ion concentrations Figs. 3 and 4 . The sorption 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

Above given order illustrates that initially equilibrium for metals uptake is more favorable for *C. nucifera*, its sorption capacity and selectivity is the same as presented in previous Table 2. The trend presented by *SF* in Fig. 5 is also providing information that the *C. nucifera* biomass is more effective and excellent adsorbent for metal at lower metal concentrations.

Table 3
Calculated separation factor (SF) for biosorption of metals

Ci	SF of Pb^{2+}	SF of Cu^{2+}	SF of Zn^{2+}	SF of Ni^{2+}
25	0.270	0.396	0.411	0.449
50	0.156	0.247	0.258	0.289
75	0.109	0.179	0.188	0.213
100	0.084	0.141	0.148	0.169
125	0.068	0.116	0.122	0.140
150	0.0581	0.098	0.104	0.119

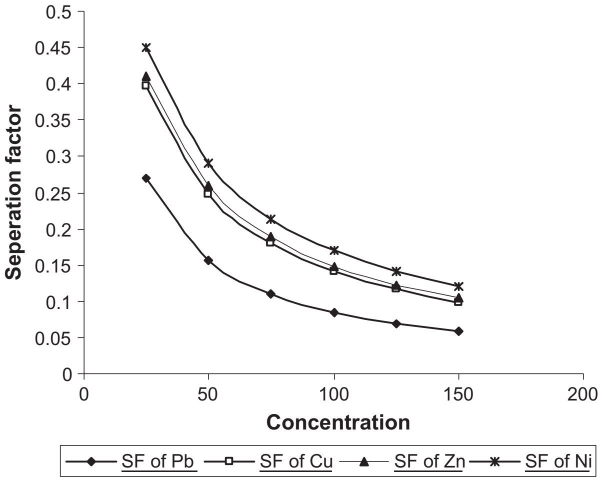


Fig. 5. Plotof separation factor (*SF*) profile for biosorption of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} on *C. nucifera* biomass.

4.2. Surface coverage (θ)

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

$$\begin{aligned} bC_i &= \theta/(1-\theta) \\ \text{and} \quad \theta &= bC_i/(1+bC_i) \end{aligned} \tag{12}$$

where *b* is the adsorption coefficient, C_i the initial concentration 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 [33]. The data are presented in Table 3. Fig. 6 shows that increase in initial metal ion concentration for *C. nucifera* biomass increases the surface coverage on the biomass until the surface is nearly fully covered with a monomolecular layer. Further examination of Fig. 6 reveals that

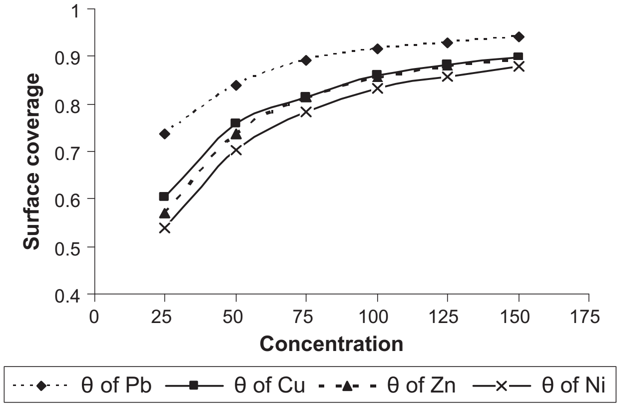
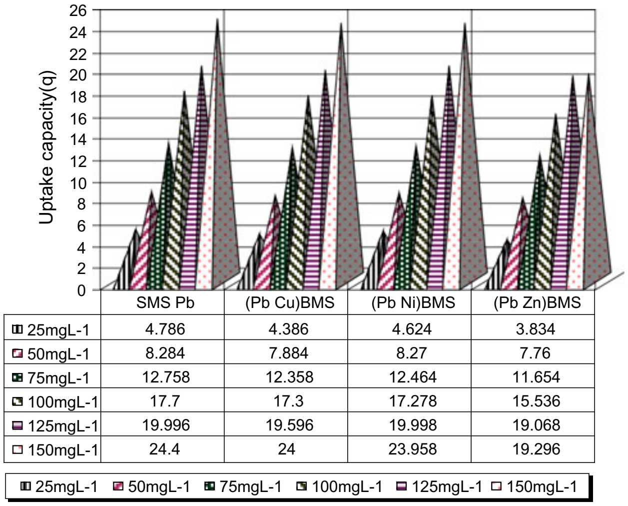
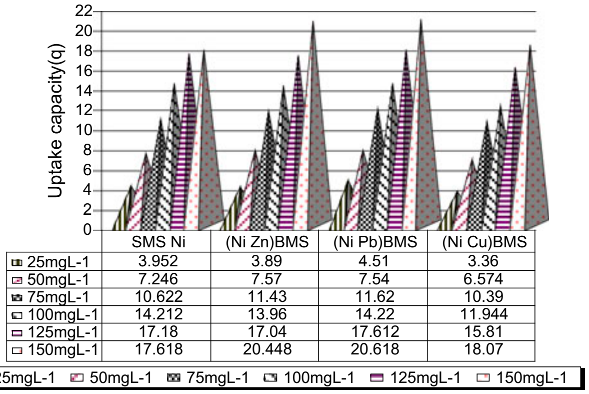


Fig. 6. Plot of surface coverage (θ) against concentration of Pb^{2+}, Cu^{2+}, Zn^{2+}, and Ni^{2+} on *C. nucifera* biomass.



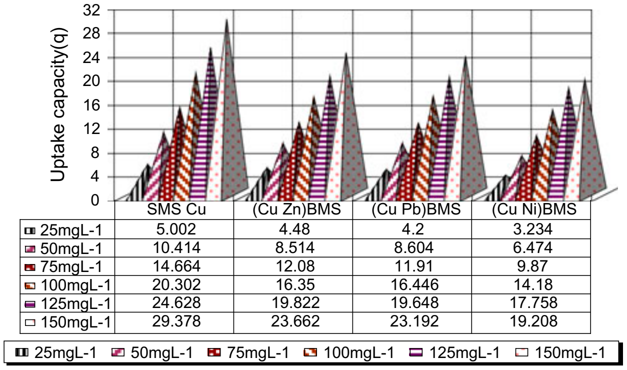
	SMS Pb	(Pb Cu)BMS	(Pb Ni)BMS	(Pb Zn)BMS
25mgL-1	4.786	4.386	4.624	3.834
50mgL-1	8.284	7.884	8.27	7.76
75mgL-1	12.758	12.358	12.464	11.654
100mgL-1	17.7	17.3	17.278	15.536
125mgL-1	19.996	19.596	19.998	19.068
150mgL-1	24.4	24	23.958	19.296

Fig. 7. Comparison of uptake capacity (q) of Pb^{2+} in SMS and BMS by *C. nucifera*.



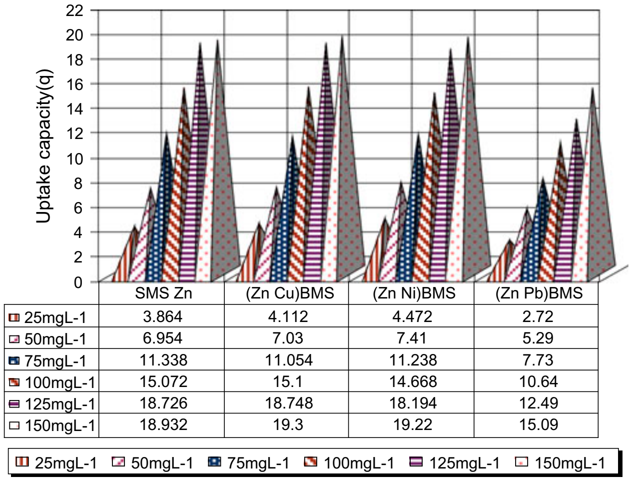
	SMS Ni	(Ni Zn)BMS	(Ni Pb)BMS	(Ni Cu)BMS
25mgL-1	3.952	3.89	4.51	3.36
50mgL-1	7.246	7.57	7.54	6.574
75mgL-1	10.622	11.43	11.62	10.39
100mgL-1	14.212	13.96	14.22	11.944
125mgL-1	17.18	17.04	17.612	15.81
150mgL-1	17.618	20.448	20.618	18.07

Fig. 8. Comparison of uptake capacity (q) of Ni^{2+} in SMS and BMS by *C. nucifera*.



	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

Fig. 9. Comparison of uptake capacity (q) of Cu^{2+} in SMS and BMS by *C. nucifera*.



	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

Fig. 10. Comparison of uptake capacity (q) of Zn^{2+} in SMS and BMS by *C. nucifera*.

Table 4
Surface coverage (θ) of metals for *C. nucifera* biomass

C_i (mg L^{-1})	θ of Pb^{2+}	θ of Cu^{2+}	θ of Zn^{2+}	θ of Ni^{2+}
25	0.737	0.603	0.568	0.540
50	0.838	0.760	0.737	0.703
75	0.891	0.814	0.815	0.782
100	0.916	0.860	0.854	0.832
125	0.929	0.882	0.878	0.858
150	0.940	0.899	0.895	0.879

the surface coverage ceases to vary significantly with concentration of metal ions at higher levels (Table. 4).

Surface coverage value for metal ions on sorbents of *C. nucifera* is in following order:

Pb > Cu >Zn > Ni

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

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