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Optimization of operational conditions for the maximum biosorption of Co (II) using *Buddleia asiatica*

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Abstract

The low-cost adsorbents are achieved from Buddleia asiatica wastes as a substitution for costly conventional methods of removing heavy metal ions from wastewater. It is renowned cellulosic waste materials can be obtained and utilized as a cheapest adsorbents and their performance to remove heavy metal ions can be affected upon chemical treatment. Major problem is contamination of environment with the heavy metals. The efficacy of Buddleia asiatica was tested for the removal of Co (II) metals using batch experiments in single and binary metal solutions under controlled experimental conditions. The stock solutions were prepared in de-ionized water for Co. Then bio sorbent dose was thoroughly mixed with varying concentrations of metal ion solutions in conical flasks for batch experiments in SMS (single metal solution) and BMS (binary metal solution). The solutions were filtered for analyzing sorbet metal concentration using flame atomic absorption spectrometry. The results were evaluated statistically by using regression method. The treated adsorbent showed good adsorption capacities for Cu.

Key words: Biosorption, Cu ion, Biomass, Wastewater, SMS, BMS

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1. Introduction

Biosorption is the term which is used to describe for the removal of heavy metals by passive binding to nonliving biomass from an aqueous solution [1] recovers the expensive metals [2]. Different plant extracts are used as bio sorbent, marine algae bacteria and fungi are also included [3,4] a powerful technique used for the elimination and recovery of heavy metals from solution [5]. It is also a process in which removal of metal ions takes place from aqueous solution by biological material [6].

In biosorption different kinds of biomasses is used, especially Algae, fungi, bacteria, industrial and agricultural byproducts and various other living materials [7]. They can also block the functional groups of very important enzymes [8]. Bio sorption is better as compared to the pervious used methods because of its highly selective efficient, easy to operate and cost effective in the treatment of large volume of water containing many toxic heavy metals [9].

A large number of mechanisms are include in the process of Bio sorption e.g. adsorption, electro static attraction, covalent binding, complexion, ion-exchange, Vander Waals' attraction and micro precipitation [10]. Acute exposure to cobalt can induce nausea, vomiting and neuro toxicological symptoms such as headaches and changes in reflexes, whereas chronic exposure can induce partial or complete loss of smell, gastrointestinal troubles and dilation of the heart which in turn, have led to strict effluent standards for cobalt. Although a number of physico-chemical technologies are available for trace metal (cobalt) removal, the costs associated with some technologies or their ineffectiveness, have resulted in bio sorption being considered as an alternative technology for trace metal removal [11].

The process of bio sorption occurs at different optimum conditions which are followings pH, temperature, primary metal concentration and bio sorbent amount [12]. Different species were used for conducting experiment for the removal of cobalt and nickel from aqueous solution [13]. The order for uptake of biomass is specific for heavy metals [14]. Bio sorption has many benefits over other procedure such as low cost, short time interval, no production of side product and many others [15].

Biosorption mostly used inexpensive biomass for the removal of heavy metals from industrial effluents [16]. Biosorption is widely used for several years to handling the large volume of waste waters [17]. The process involves physical and chemical methods which include diffusion, adsorption, chelation, complexion, coordination or micro precipitation mechanisms.

Heavy metals such Co is main component of industrial effluents. Its small quantity may be detrimental and causes hazardous effect. Adsorption is one of the technologies which are used for the removal of these toxic materials [18]. Bio sorption is also a physiochemical process that naturally biomass which allows it to passing concentrates on to its cellular structure. The essential elements needed to dead biomass for their growth available as by product or waste [19].

A range of various naturally occurring biological materials such as bacteria, fungi, mosses, algae, macro-phytes and higher plant can reduce the concentration of Co and Ni from aqueous solution from ppt to a level of ppb [20]. A suitable bio sorbent can be effectively used for the removal of heavy metal from industrial aqueous solution. The major benefits of this process are that it reduces the concentration of heavy metal to a permissible level [21].

The process of biosorption is based on the ability of microorganisms that they adsorb heavy metal from aqueous solution through a number physical-chemical ways. This is occurring through the cell's wall. Biomass metabolism does not always involve in this process so, it does not influence that microorganisms are dead or alive for the progress of this process [22]. These plants produce fruits and also edible leaves these remain whole year. In India it is cultivated on large scale; it produces a large amount of bark. The bark of these plants however contain large amount of nutrients, vitamins, amino acid and fatty acid [10].

Cobalt containing compounds are widely used in many industries including the petrochemical industry [23]. Cobalt present in industrial wastewaters can produce a variety of undesirable effects on humans [24]. The most appropriate amount of Co in drinking water is $0.5 mgL^{-1}$ [25]. But high dose of Co is also harmful. Excess amount of cobalt also caused respiratory disorders, injury of the pancreas, arteriosclerosis, leukopenia, hypocupremia, lymph-adenopathy, hypoferremia and neutropenia [26]. High amount of copper is also responsible for many diseases such as brain, pancreas, skin and many heart diseases [27].

In this research work, dried biomass of Buddleia asiatica was used. The main purpose of present research work was to study the bio sorption of Co (II) using (*Buddleia asiatica*) biomass to develop a cost effective process. The effect of different parameters like pH and metal ion concentration were studied and discussed below.

Mechanism of Biosorption

According to the location bio sorption can be classified in to three components which are

a. Extracellular precipitation
b. Cell surface sorption
c. Intracellular accumulation.

The plant Buddleia asiatica was hardy to zone 8. It has been used as an abortifacient and also in the treatment of skin complaints. The juice of the plant is applied as a wash to treat skin diseases. It could be used for making sticks. The biosorption capacity of bio sorbents can be increased by different pretreatments.

Biosorption commonly occurs on the surface of the bio sorbent and increasing the number of binding sites on the surface of the bio sorbent may prove an effective approach to enhancing biosorption [21]. Immobilization of biomass has also been found to be among the better techniques for making bio sorbent suitable for process application. The focus of this research was to evaluate the bio sorption capacity of metal Co and to evaluate the effect of pH and different metal ion concentration.

2. Material and Methods

2.1 Chemicals

The chemicals used in this investigation for experimentation and other purposes are: Cobalt Nitrate ($(Co(NO_3)_2.6H_2O)$, Nitric acid (HNO_3), Sulphuric acid (H_2SO_4), Hydrochloric acid (HCl) and Sodium hydroxide (NaOH) were of laboratory grade. Buddleia asiatica used as biomass for the bio sorption of Co (II) in synthetic solutions. Biosorbent was collected from local market of Faisalabad.

2.2 Preparation of biomass

The collected biomass was extensively washed with distilled water to remove impurities, dust and particulate material from their surface and then shed drying. Dried biomass was cut, crushed, ground and then use in for the formation of metal solution.

2.3 Preparation of stock Co (II) solution

Salt of Co (II) ($Co(NO_3)_2.6H_2O$) was used as adsorbates.1000ppm solution of Co (II) was prepared by dissolving 1g Cobalt Nitrate ($Co(NO_3)_2.6H_2O$) in 1000mL of distilled water. Working solution (100ppm) was prepared by dilution of stock solution having concentration of

1000ppm with distilled water. The stock solution was stored in measuring flask.

2.4 Batch studies of SMS

For SMS(single metal solution), solutions of fixed volume (100 mL) with varying concentrations in conical flasks were thoroughly mixed with 0.5 g of bio sorbent dose, size of 255 to 355 micron at 30°C and 100 revolutions per minute (rpm) shaking speed for 12 hours. Twelve hours of equilibrium period for sorption experiment was used to ensure equilibrium after conducting equilibrium studies of the bio sorbent. The pH range was adjust from 4-6 by using 0.1M HNO_3 and 0.1M 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.

2.5 Batch studies of BMS

For BMS (binary metal solution) 100 mL volume of solutions with varying concentrations (25, 50, 75, 100, 125 and 150 mg L^{-1}) of main metal and 25 mgL^{-1} of affecting metal concentration in the same solution in conical flasks were thoroughly mixed under same conditions stated for SMS solutions. The solution was separated from the biomass by filtration through filter paper. Filtrates of SMS and BMS was diluted to 10 mg/L or 20 mg/L with deionized water and analyzed for metal concentration using flame atomic absorption spectrometry. Biosorption capacities were calculated for each concentration by obtained readings of Atomic Absorption Spectrophotometer (AAS).

2.6 Equilibrium modeling

Metal ions bio sorption can be studied by two types of isotherms such as Langmuir model, in which the amount of metal uptake by biomass reaches equilibrium and the Freundlich model, in which the amount of metal uptake by biomass increases with time. Freundlich and Langmuir adsorption isotherms were applied to describe the equilibrium relationships between sorbent and sorbet in solution [28]. Sorption equilibrium is established when the concentration of sorbet in the bulk solution is dynamic balance with that of the interface. The expression of this relationship is termed as bio sorption isotherm, of which the Langmuir and Freundlich equations are most widely used [29]. The Langmuir and Freundlich adsorption constants evaluated from the isotherms with correlation coefficients [30].

2.7 Langmuir isotherm

For Langmuir isotherm, following assumptions is valid specifically for the simplest case [31].

1. The surface containing the adsorbing sites is perfectly flat plane with no corrugations (assume the surface is homogeneous).
2. The adsorbing gas adsorbs into an immobile state.
3. All sites are equivalent.
4. Each site can hold at most one molecule of a (mono-layer coverage only).
5. There are no interactions between adsorb ate molecules on adjacent sites.

The general form of Langmuir isotherm equation is written as [32].

$$1/qe= 1/qmax + 1/ (b\ qmax)\ Ce$$

Where

- qe = equilibrium adsorption capacity
- Ce = equilibrium concentration
- 1/qmax = constants
- b = constants

Both constants obtained from regression equation, Called intercept and slope respectively [33].

2.8 Freundlich isotherm

General form of Freundlich isotherm is written as

$$[qe = K\ Ce\ 1/n]$$

The Freundlich isotherm equation assumes that a bilayer sorption with a heterogeneous energetic distribution of active sites, accompanied by interaction between adsorbed molecules [33]. Freundlich is other equation is an empirical relationship describing the adsorption of solutes from a liquid to a solid surface.

The linearized form of Freundlich isotherm equation is written as

$$\text{Log } qe = \log Kf + (1/n) \log Ce$$

Where

- Ce = equilibrium concentration
- qe = amount of metal ions adsorbed per specified amount of adsorbent at equilibrium
- Kf = Constant
- 1/n = Constant

Both constants obtained from regression equation, called intercept and slope respectively.

Graph was plotted log qe verses log Ce. The slopes and intercepts of the graph were used to calculate the 1/n and Kf values. Kf is a measure of the degree or strength of adsorption, while 1/n is used as an indication whether adsorption remain constant or decreased with increasing adsorb ate concentration [35].

2.9 Bio sorption capacity of Co (II)

Uptake of Co (II) was calculated from an equation

$$q = \frac{V\ (C_i - C_f)}{M}$$

Here

- q = Co (II) uptake capacity (mg/g)
- C_i=Initial metal concentration of Co (II) in solution (mg/L)
- C_f = Final metal concentration of Co (II) in solution (mg/L)
- V = Solution volume (mL)

3. Results and Discussion

Current research activity is focused on evaluating, whether bio sorption may eventually provide such an affective and economic alternative treatment process, while biological treatment is reasonably effective in removing organic pollutants, heavy metals however tend to accumulate in biological sludge, which is unfit as fertilizers and require incineration for its disposal. Biosorption is a relatively new process that utilizes inactive biomass which showed significant contribution for the removal of contaminants from aqueous effluents [1]. The presence of key functional groups on the biomass cell walls is responsible for their outstanding metal sorbing properties [33].

3.1 Effect of different pH values on Ni (II) bio sorption using Buddleia asiatica

Different metal ions may have different pH optima, possibly due to different solution chemistry of the species. Solution pH is an important parameter which affects the bio sorption of heavy metals. In this research work different pH (2, 3, 4, 5 and 6) medium were selected while all other operational parameters were kept constant. The pH of metal solution play an important role in the process of bio sorption and the rate and extent of metal bio sorption may decrease with external low pH medium. It is observed that metal removal at low pH values is comparatively less with higher pH mediums for both with leaves and stems [35]. Results of metal removal at different pH mediums were depicted in the table 1.

Sorption of metal ions on adsorbents is strongly dependent on solution pH. The pH of the aqueous medium not only affects the solubility of the metal ions but also the ionic form in which it will be present in the solution and the type and ionic state of the functional groups at the bio sorbent surface. At low pH, adsorption sites are more protonated and they are less attractive against to various cationic forms of metals. Depending on hydrolysis constant of a specific metal, in the solution having pH more than a specified value, various aqueous speciations of metals due to hydrolysis will affect the approach of metal species [36].

3.2 Effect of metal ion concentration on the bio sorption

Bio sorbent is an important parameter for the optimization of bio sorption system. The effect of metal ion concentration on the removal of Co (II) from the aqueous solution by using *Buddleia asiatica* is studied. Table 2 showed the relation between metal uptakes of capacities q (mgg^{-1}) and the metal ion concentration (mg/g) for the removal of Co (II). Results showed that sorption capacity increased with increased in initial metal ion concentration of Co (II) on the biomass and % age removal decreased with increased in initial metal concentration [29].

The increase in sorption capacity may be explained by the fact that at low concentration, the available metal occupies adsorption sites more quickly [37]. However, at higher concentrations metal ion diffuses to biomass surface [38].

The initial metal concentration provides an important force to overcome all mass transfer resistance of metal ions between the aqueous and solid phase, hence a higher initial concentration of metal ions may increase the adsorption capacity and decrease the percentage adsorption of dried biomass. All the bio-sorbents has a limited number of active sites, which would become saturated at a certain concentration [39]. It can be explained by the fact that at very low concentration of metal ions, the ratio of sorption surface area to the total metal ions available is high and there is a greater chances for metal removal. At high concentration low adsorption is due to the saturation of adsorption sites [29].

3.3 Adsorption isotherm

The adsorption isotherm models (Langmuir and Freundlich isotherms) were followed to measure the interaction of metal ions with biosorbent as shown in Table 4. It is cleared from the data the values of n and K_f for both leaves and stem are higher than the reported that higher the values of K_f and n than K indicated that higher the affinity of metal ions with the bio sorbent. The values of Freundlich exponent n were higher than unity indicating that captions are favorably attracted towards bio sorbent. The correlation coefficient (R^2) for bio sorption studies indicate that used models are most suitable and applicable for explaining these sorption processes. The data further showed that bio sorption of two divalent metals on to the biomass increased with increase in initial metal ion concentration.

In Fig 3 and Fig 4 the graph (a) and (b) shows the effect of metal ion concentration by applying Langmuir model which does not fit on these values while in Fig 5 the graph (c) and (d) shows the Freundlich model in which concentration of Ce increases slowly and then becomes constant and it is fit on these values. This is binary metal sorption (BMS) [40].

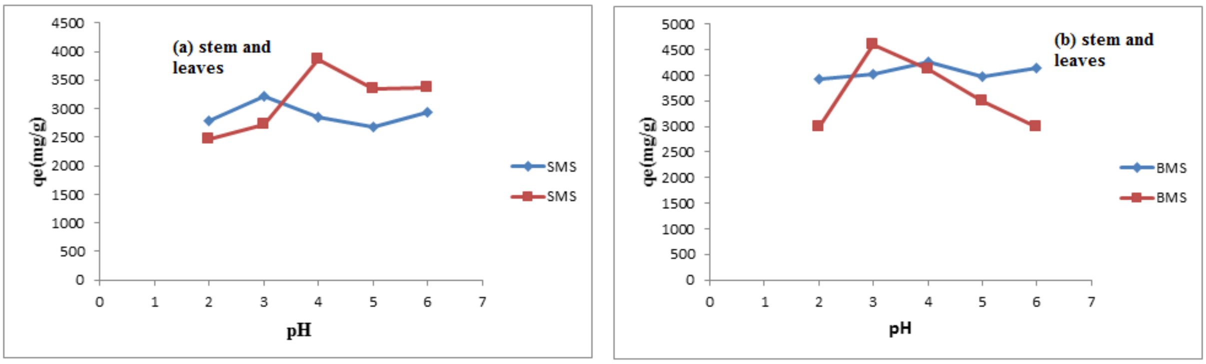

Fig.1 Effect of pH on leaves of *Buddleia asiatica* (a) SMS and (b) BMS

Table.1 Effect of pH on the biosorption of Co (II) with leaves and stems of plant *Buddleia asiatica*. (SMS)

Biosorbent	pH	$C_i(mgL^{-1})$	$C_e(mgL^{-1})$	$q(mgg^{-1})$	% Removal
Co (with leaves)	2	50	22.22	2778	55.5
	3	50	17.79	3221	64.4
	4	50	21.58	2842	56.8
	5	50	23.12	2688	53.7
	6	50	20.07	2930	59.8
Co (with stem)	2	50	25.34	2466	49.3
	3	50	22.69	2731	54.6
	4	50	16.41	3859	67.1
	5	50	16.45	3355	67.1
	6	50	11.41	3359	77.1

Table.2 Effect of pH on biosorption of Co (II) with leaves and stems of plant *Buddleia asiatica* (BMS)

Bio-sorbent	pH	$C_i(mgL^{-1})$	$C_e(mgL^{-1})$	$q\ (mgg^{-1})$	% removal
BMS (Co and) (with Leaves)	2	50	10.68	3932	78.6
	3	50	9.87	4013	80.2
	4	50	10.24	4271	79.5
	5	50	8.46	3976	83.0
	6	50	7.29	4154	85.4
(with Stem)	2	50	14.53	3000	70.9
	3	50	6.95	4600	86.1
	4	50	8.70	4130	82.6
	5	50	4.40	3500	93.2
	6	50	4.00	3000	92

Table.3 Effect of different metal ion concentration on the bio sorption of Co (II) with leaves and stems of plant *Buddleia asiatica*. (SMS)

Bio sorbent	$C_i (mgL^{-1})$	$C_e (mgL^{-1})$	$q\ (mgg^{-1})$	% removal
Co (with Leaves)	10	3.9	540	92
	20	8.9	640	81
	30	13.7	810	76
	40	17.6	1700	72
	50	24	1860	65
	60	29	2330	60
	70	35.5	4130	52
	80	40.1	6000	45
	90	46	6010	43
	100	50	6010	42
Co (with Stem)	10	7.2	17.8	44
	20	17	36	57
	30	41	61	76
	40	113	88	55
	50	232	170	64
	60	390	250	81
	70	517	380	43
	80	690	500	52
	90	780	750	41
	100	900	750	39.5

Table.4 Effect of different metal ion concentration on the bio sorption of Co (II) with leaves and stems of plant *Buddleia asiatica*. (BMS)

Bio sorbent	$C_i (mgL^{-1})$	$C_e (mgL^{-1})$	$q\ (mgg^{-1})$	% removal
Co (with Leaves)	10	3.9	540	92
	20	8.9	640	81
	30	13.7	810	76
	40	17.6	1700	72
	50	24	1860	65
	60	29	2330	60
	70	35.5	4130	52
	80	40.1	6000	45
	90	46	6010	43
	100	50	6010	42
Co (with Stem)	10	7.2	17.8	64
	20	17	36	67
	30	41	61	76
	40	113	88	55
	50	232	170	64
	60	390	250	51
	70	517	380	43
	80	690	500	52
	90	780	750	81
	100	900	750	39.5

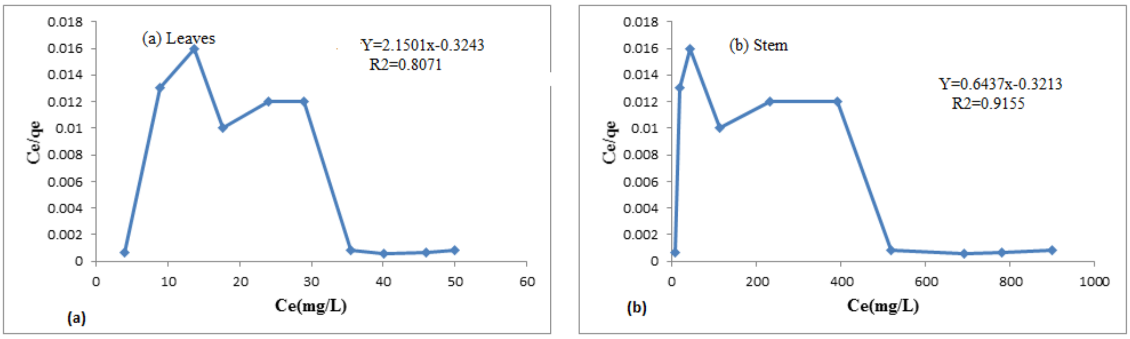

Fig.2 Langmuir isotherm of (a) leaves and (b) stem of *Buddleia asiatica*

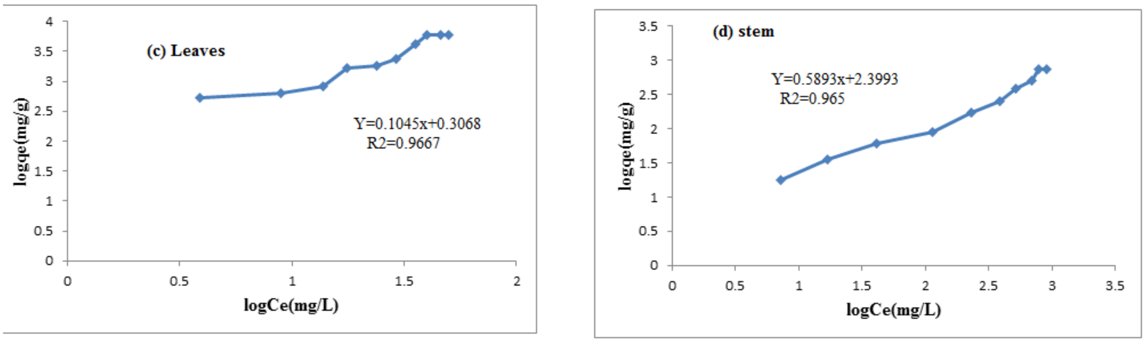

Fig.3 Frendulic isotherm of (a) leaves and (b) stem of *Buddleia asiatica* (SMS)

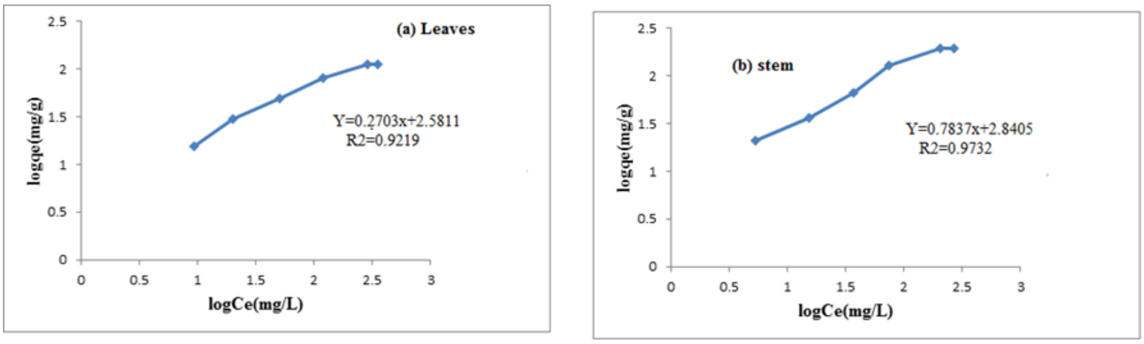

Fig.4 Freundlich isotherm of (a) leaves and (b) stem of *Buddleia asiatica* (BMS)

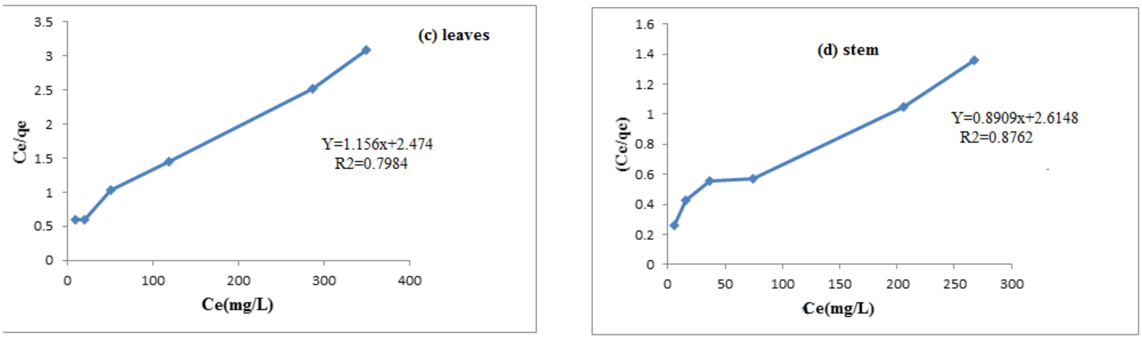

Fig.5 Langmuir model of (c) leaves and (d) stem of plant *Buddleia asiatica* (BMS)

Table.5 Comparison between kinetic models for the biosorption of Co (II) and Ni (II) using plant *Buddleia asiatica*

Metal	Biosorption	Langmuir Model			Experimental value	Freundlich Model			
		X_m	K_L	R^2		q_{max}	1/n	K_F	R^2
		(mg/g)	(L/mg)	-	q (mg/g)	(mg/g)	-	(mg/g)	-
Co (II)	SMS	85.23	12.65	0.912	3.77	3.73	0.905	1.871	0.901
		90.90	14.271	0.988	2.87	2.77	0.748	0.563	0.971
	BMS	3.92	4.99	0.920	3.69	3.65	0.679	0.272	0.921
		125	16.25	0.996	3.47	3.45	0.340	0.664	0.941

4. Conclusion

This study showed that the increase in sorption capacity may be explained by the fact that at low concentration, the available metal occupies adsorption sites more quickly. However, at higher concentrations metal ion diffuse to the biomass surface. In the same way at specific pH the metals show maximum absorption.

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