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Utilization of *Mentha arvensis* waste biomass for the removal of Pb (II) and Co(II) from aqueous solutions

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ABSTRACT

This paper reports on the potential utility of *Mentha arvensis* for the removal of Pb(II) and Co(II) ions from simulated water samples. Maximum biosorption capacity value of 111.97 and 116.93 mg/g was obtained for Pb(II) and Co(II), respectively. Triton X-100-treated biomass showed remarkable increase in the biosorption capacity of biomass for Pb(II) and HCl treated for Co(II) ions, respectively. The influence of solution pH, biosorbent dose, metal ions concentration, particle size of biosorbent, and contact time on the biosorption process was also studied. Batch biosorption equilibrium data were fitted to both Langmuir and Freundlich adsorption isotherms, but the Langmuir had a better fit with the results. Reaction kinetics was best described by pseudo-second-order kinetic model. The biosorption capacity of waste biomass decreased with an increase in the temperature indicating exothermic nature of the biosorption. Fourier transform infrared spectroscopy (FT-IR) and scanning electron microscopy (SEM) analyses were carried out to examine functional groups and surface morphology of biomass. Results indicated that biosorption of the Pb(II) and Co(II) ions onto *M. arvensis* is an economical and environment-friendly method for wastewater treatment.

Keywords: Mentha arvensis; Treatment; Biosorption; Metal ions; Wastewater

1. Introduction

Ecological pollution with toxic heavy metal ions by massive increase in industrialization and urbanization is one of the foremost concerns of the current century. Heavy toxic metal ions accumulate in the food chain due to their persistent, nonbiodegradable, and carcinogenic nature, causing a number of disorders in human beings as chronic and acute ailments [1,2]. Wastewater treatment for the removal of pollutants, especially toxic heavy metals ions, remains a challenge to both developed and developing countries of the world.

Different conventional technologies as precipitation, coagulation, ion exchange, ultra filtration, and adsorption have been in use for the removal of noxious heavy metal ions from aqueous systems up to acceptable safe limit, suggested by many organizations as World Health Organization (WHO) and Environmental Protection Agency (EPA) [3–5]. Disadvantages associated with these methods are as costly equipments, operational cost, toxic sludge production, and space requirements [6]. A number of advantages associated with biosorption over other conventional techniques include simple and toxic sludge-free operation, low cost, and high selectivity [7].

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Lead, one of the nonessential metal ions, is the third most toxic priority metal pollutant [8] listed by EPA and directly enters into water bodies through the effluent discharges including lead storage battery manufacturing, paper and pulp industries, mining operations, and smelting and metallurgical finishing processes [9–12]. Extensive reports and reviews are available on the toxicity of lead due to its excessive intake leading to immunological, neurological, developmental, reproductive, genotoxic, and carcinogenic effects. The permissible limit for lead ions in drinking water and wastewater as suggested by EPA is 0.05 mg/L and 0.1 mg/L, respectively [11,13].

Cobalt is one of the common toxic heavy metals, disseminated in the environment via wastewater of nuclear power plants and many other industries such as mining, metallurgical, electroplating, paints, pigments, and electronic industries [14]. Several health troubles such as paralysis, diarrhea, low blood pressure, lungs irritation, and bone defects result in human beings due to frequent exposure. The standard level of cobalt in drinking water is 2 μg/L but values up to 107 μg/L have been reported. The permissible limit of cobalt in industrial effluents is 0.5 mg/L [15,16].

Biosorption is potential and attractive technology for treatment of wastewater. Biomasses have the ability to adsorb metal ions due to different functional groups of macromolecules such as polysaccharides, proteins, and lignin [10,17]. The biosorption of metal ions to the biomass surface occurs mainly as a result of either physical binding involving London forces or electrostatic attraction, or chemical binding such as binding between the adsorbent and the adsorbate [11].

In recent years, number of waste biomasses such as bagasse, sawdust, pine bark, tree fern, spent grain, corn cobs, apple residue, hazelnut shells, coconut husk, rice husk, coconut coir husk, coir pith carbon, potato peels, peat, tea leaves, orange peel, cocoa shell, olive stone, walnut, hazelnuts, almond shells, barley straw, lotus stalks, and grape stalk have been employed for the removal of toxic heavy metal ions and dyes from aqueous media [17–19], but high volumes of wastewater, still demands exploration of newer adsorbents.

Mentha arvensis, generally recognized as menthol mint or kitchen herb, belongs to the family *Lamiaceae*, a group of aromatic herbs having significant economic importance as essential oil source. The commercial importance of mint is well known as natural antioxidant. The anti-mycotic effect of mint oil has also been reported.

The objective of the present research work was to examine the biosorption capacity of waste biomass i.e. *M. arvensis*, and explore it as cost effective and efficient biosorbent for target metal pollutants i.e. Pb(II) and Co(II), which are commonly found in industrial effluents.

2. Materials and methods

2.1. Chemicals

All chemicals and reagents used were of analytical grade and were used further without any refinement. $Pb(NO_3)_2$, $Co(NO_3)_2$, H_2SO_4, HCl, NaOH, Triton X-100, acetone, and acetic acid were purchased from Merk, Germany. Atomic absorption spectrometric standard solutions for Pb(II) and Co(II) were obtained from Sigma-Aldrich, Chemical Co., USA.

2.2. *M. arvensis* biomass

M. arvensis waste biomass used in the present study was obtained free of cost from Rose Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. The biomass was at first extensively washed with double distilled water (DDW) to remove soluble particulate material from surface and after sun drying, the biomass was subjected to oven drying at 50–60°C for 72 h. Dried biomass was sieved through octagon siever (OCT-DIGITAL 4527-01). This was done to remove any large size particle and to obtain adsorbent with a known particle size (0.25–1 mm).

2.3. Biosorbent characterization

Biomass of *M. arvensis* was coated under vacuum with a thin layer of gold, which was examined by scanning electron microscopy (JEOL, JSM-6400, Japan) to study surface morphology. The FT-IR (IR Perkin Elmer 1600 spectrometer) analysis of biomass was carried out to determine chemical functional groups, responsible for sorption of metal ions. The IR data were observed over 400–4,000 cm^{-1} by preparing KBr disks of biosorbent material, and spectra were recorded on software Bio-Rad Merlin.

2.4. Chemical treatments of biomass

Chemical treatments of biomass may enhance or decrease the biosorption capacity of the biomass. In order to observe the effect of different chemicals like HCl, NaOH, acetone, acetic acid, and Triton X-100, 1 g of biomass/25 mL of 1 M reagent was soaked for 24 h. Then, suspensions were extensively washed with DDW and filtered thoroughly until a pH 7 ± 0.1 of treated biomass was attained. Finally, the resulting biomass was air-dried.

2.5. Pb(II) and Co(II) solutions

Stock Pb(II) and Co(II) solutions (1,000 mg/L) of pH 5.0 and 6.0 were prepared by dissolving 1.598 g $Pb(NO_3)_2$ and 3.10 g $Co(NO_3)_2$ in 100 mL of DDW and diluting it up to 1,000 mL quantitatively using DDW, respectively [20]. Solutions of different concentrations were prepared by adequate dilution of the stock solution with DDW. Glassware and polypropylene flasks used were immersed overnight in 10% (v/v) HNO_3 and rinsed several times with DDW. Both Pb (II) and Co(II) solutions were separately used, and independent optimization of process parameters was investigated.

2.6. Batch biosorption studies

Batch biosorption studies were carried out in 250 mL conical flasks containing 100 mL of Pb(II) and Co(II) (100 mg/L) solutions of known pH and biosorbent amount (0.1 g) of known particle size (0.25 mm). Conical flasks were over sealed with aluminum foil. The solutions were agitated on orbital shaker incubator at 130 rpm for 24 h at 30℃ temperature. After 24 h, samples were filtered and stored in sample bottles at room temperature (30℃). All biosorption affecting parameters in batch mode i.e. pH, biosorbent dose, biosorbent size, adsorbate concentration, temperature, and incubation time were optimized by studying over a certain range of these parameters.

2.7. Determination of the Pb(II) and Co(II) contents in the solutions

The concentration of Pb(II) and Co(II) ions in the solutions before and after the equilibrium was determined by flame atomic absorption spectrometry (FAAS), using a Perkin Elmer AAnalyst 300 atomic absorption spectrometer equipped with an air–acetylene burner and controlled by Intel Pentium 4 personal computer. The hollow cathode lamp was operated at analytical wavelength of 283.3 nm for Pb (II) and 240.7 nm for Co(II) and slit as 0.2 nm for both metal ions [11].

2.8. Calculation of Pb(II) and Co(II) uptake from solutions

The Pb(II) and Co(II) uptake was calculated by the simple concentration difference method. The initial concentration C_i (mg/L) and metal concentrations at various time intervals C_e (mg/L), respectively, were determined, and the metal uptake q (mg metal adsorbed/g adsorbent) was calculated from the mass balance as follows:

$$q = (C_i - C_e) \times V/W \tag{1}$$

where V is the volume of the solution in L and W is the mass of the biosorbent in g.

$$\%\ \text{Biosorption} = (C_i - C_e)/C_i \times 100 \tag{2}$$

2.9. Statistical analysis

Each experiment was conducted in triplicate to ensure the reproducibility of results. All data represent the mean of three independent experiments. Statistical analyses were performed using the statistical functions of Microsoft Excel version Office Xp (Microsoft Cooperation, USA).

3. Results and discussion

3.1. FT-IR and SEM studies

The FT-IR technique is very helpful in identifying important functional groups, which are responsible for biosorption of metal ions. The IR radiation interaction with the biomass causes different vibrations in chemical bonds as stretching and bending resulting in IR radiation absorption in specific range of wave length. The possible functional groups helpful in sorption are presented in Fig. 1. The spectral peaks at 3500–3000 cm^{-1} due to NH are stretching and NH bending vibrations. Carboxylic acids display a broad intense –OH stretching absorption from 3000 to 2500 cm^{-1}, phosphine (2349.30 cm^{-1}), carbonyl (1685.39 cm^{-1}), primary amines (1593.20 cm^{-1}), secondary amine (1531.48 cm^{-1}), esters (1292.31 cm^{-1}), ethers (1016.49 cm^{-1}), thioesters (894.97 cm^{-1}), and alkyne (663.51 cm^{-1}). The analysis of FTIR spectrum showed the presence of ionizable groups (carboxyl, amino, amide, and hydroxyl) on the surface of biomass, which are able to bind with protons or metal ions [20].

Surface studies of pore structure and shape of the biosorbents are done commonly by scanning electron microscopy (SEM). Highly porous biomasses show more biosorption capacity. Scanning electron micrograph of *M. arvensis* waste biomass is shown in Fig. 2, demonstrating the presence of cylindrical structures. Hollow cavities with irregular surfaces and many micropores in the periphery of the biosorbent due to high porosity on the surface reveal that *M. arvensis* would be an efficient biomass.

3.2. Effect of pH on biosorption of lead and cobalt

The equilibrium metal uptake of the *M. arvensis* from Pb(II) and Co(II) solutions (100 mg/L) at various

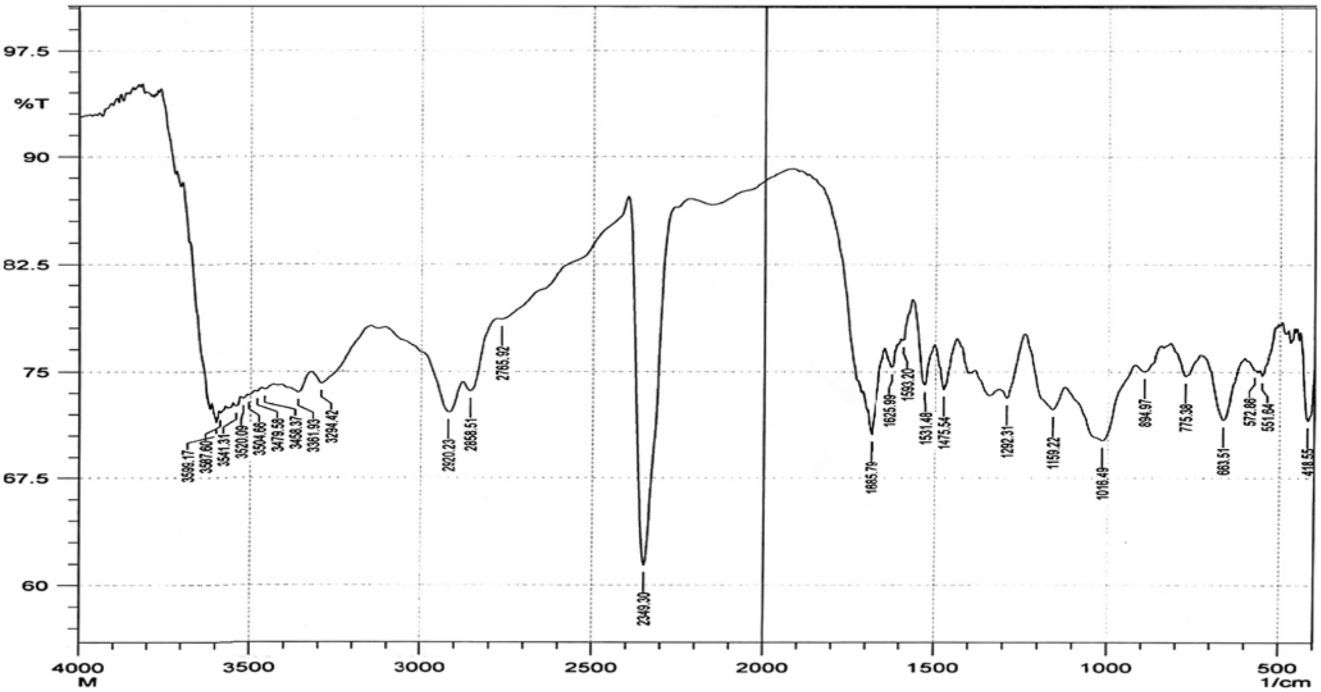

Fig. 1. FTIR spectrum of *Mentha arvensis* waste biomass.

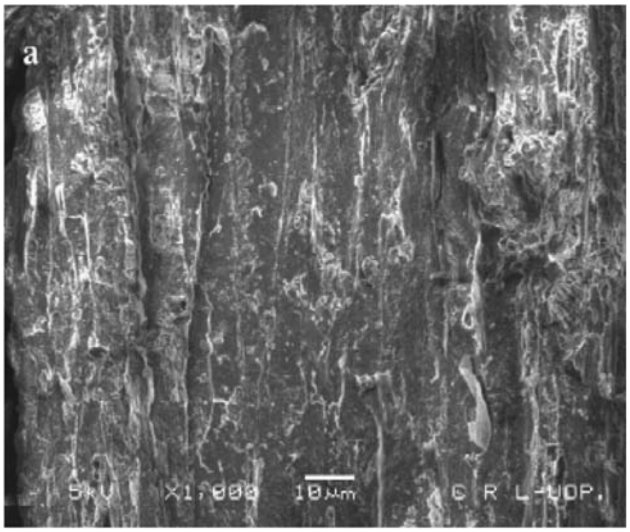

Fig. 2. SEM image of *M. arvensis* biomass.

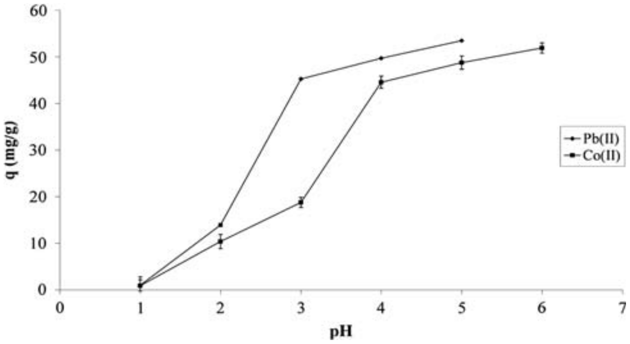

Fig. 3. Effect of pH on biosorption of Pb(II) and Co(II) ions from aqueous solution by *Mentha arvensis* waste biomass.

pH values is shown in Fig. 3. The biosorption of metal as a function of initial pH shows clearly that solution pH played a vital role in the biosorption of Pb(II) and Co(II). pH is an important parameter for biosorption of heavy metal ions from aqueous solution as it affects the solubility of metal ions and concentration of counter ions on the biomass cell walls [21]. The results show that the trend of adsorption is same for both the metal ions, however, the adsorption of Pb(II) is better than Co(II). Since different metal ions have a specific ionic size and solution chemistry, hence their adsorption is usually different. That is why trend is the same but biosorption capacity is different. Pb(II) data also have deviation but the magnitude is so small that it appears within the legends. Under highly acidic conditions, there was very little biosorption of both metal ions. A decrease in biosorption of Pb(II) and Co(II) above pH 5 and 6 is due to precipitation [22]. The optimum pH for Pb(II) and Co(II) are 5 and 6, respectively. So, it has been found that biosorption capacity values for Pb(II) is 53.47 mg/g for Co 51.88 mg/g at optimum pHs, and percentage removal of lead and cobalt are 53.47 and 51.88, respectively.

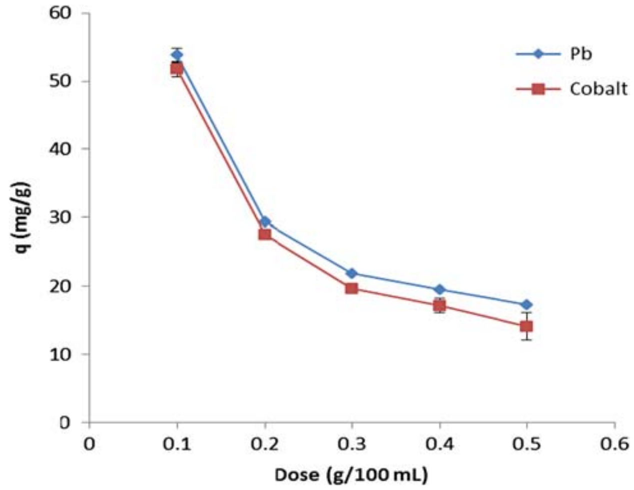

Fig. 4. Effect of biosorbent dosage on the biosorption of Pb (II) and Co(II) ions from aqueous solution by *Mentha arvensis* waste biomass.

3.3. Effect of biosorbent dose

The effect of biosorbent dose on Pb(II) and Co(II) is presented in Fig. 4. The experimental results indicated that biosorbent dose influences the Pb(II) and Co(II) uptake capacity of *M. arvensis* waste biomass. A dosage of 0.1 g/100 mL was enough for the maximum uptake of Pb(II) and Co(II) from aqueous solution. On increasing biomass concentration further, the removal of Pb(II) and Co(II) decreased, which may be attributed to overlapping or aggregation of adsorption sites resulting in a decrease in the total adsorbent area [23].

3.4. Effect of biosorbent size

Effect of biosorbent size is an important parameter in biosorption process. A particular size of biosorbent is very important as it provides definite number of functional group moieties for metal ions [23]. A definite size of biosorbent is very important as too large or small particle size decreases the interaction between biosorbent and adsorbate leading to low efficacy of the process. The influence of biosorbent size on Pb(II) and Co(II) can be evaluated from Fig. 5. The effect of altering the particle size on the Pb(II) and Co(II) uptake by *M. arvensis* waste biomass showed that there was a more dominate removal of metal ions by smaller particles as depicted from Fig. 3. This was most probably due to the increase in total surface area [24].

3.5. Effect of initial Pb(II) and Co(II) concentrations

Different metal ions have different biosorption capacities at either low concentration or high concentration. Biosorption characteristics indicate that the surface saturation depends on initial metal ions concentration [25]. Maximum biosorption capacity of Pb (II) and Co(II) ions was observed in a solution with initial metal concentration of 800 mg/L as shown in Fig. 6. In other words, we can say that the biosorption capacity of Pb(II) and Co(II) increased with the increasing value of concentration but the percentage removal of both these metals decreased with the increase in concentration. The reason for the more biosorption at high concentration may be due to availability of more surface area and functional groups for metal ions [20].

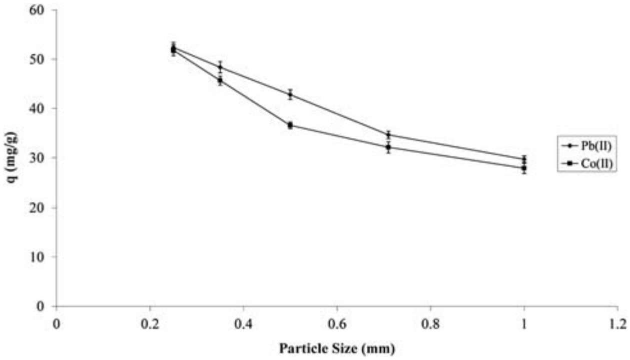

Fig. 5. Effect of biosorbent size on biosorption of Pb(II) and Co(II) ions from aqueous solutions by *Mentha arvensis* waste biomass.

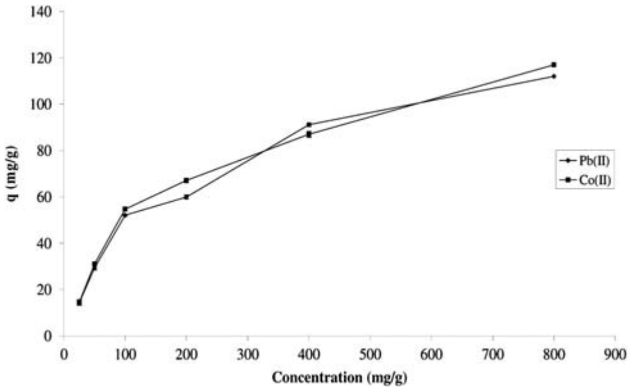

Fig. 6. Effect of initial metal ion concentration on biosorption of Pb(II) and Co(II) ions from aqueous solutions by *Mentha arvensis* waste biomass.

3.6. Adsorption isotherms

Modeling of equilibrium data was done by using most widely used Langmuir and Freundlich isotherm models. The Freundlich relationship is an empirical equation. It does not indicate a finite uptake capacity

Table 1
Comparison of Langmuir and Freundlich isotherm parameters for Pb(II) and Co(II) uptake by *Mentha arvensis* waste biomass (30˚C)

Metals	Langmuir isotherm parameters			Experiment value	Freundlich isotherm parameters			
	$q_{\max}$ (mg/g)	K_L (L/mg)	R^2	$q_{\max}$ (mg/g)	$q_{\max}$ (mg/g)	K (mg/g)	$1/n$	R^2
Pb(II)	123.46	1.08×10^{-2}	0.984	111.97	55.75	6.44	0.4573	0.918
Co(II)	128.21	1.09×10^{-2}	0.982	116.93	59.12	6.78	0.4508	0.913

of the adsorbent and thus only be reasonably applied in the low to intermediate concentration ranges. However, it is easier to handle mathematically in more complex calculations where it may appear quite frequently [20]. The heterogeneous adsorption capacity, q_e, of *M. arvensis* biomass for Pb(II) and Co(II) was determined by the following equation of Freundlich isotherm:

$$\log q_e = 1/n \log C_e + \log K \tag{3}$$

The results indicated that the equilibrium data did not fit well to the Freundlich model due to low value of correlation coefficient (Table 1).

The Langmuir isotherm considers biosorption as a chemical phenomenon. It was first theoretically examined in the adsorption of gases on solid surfaces. In the Langmuir model, maximum monolayer adsorption capacity, $q_{\max}$, (mg/g) and other parameters were determined from the following linearized equation given below:

$$C_e/q_e = 1/q_{\max}K_L + C_e/q_{\max} \tag{4}$$

where q_e is the metal ion biosorbed (mg/g), C_e is the equilibrium concentration of metal ions solution, and K_L is the Langmuir adsorption constant. Values of K_L and n indicated that Langmuir isotherm model is applicable because R^2 value is 0.984 and 0.982 for Pb(II) and Co(II), respectively, as depicted in Table 1.

3.7. Kinetic modeling of data

A kinetic study with different time intervals with fixed metal ions concentration, biosorbent amount, and biosorbent size was performed. The biosorption capacities (q) of *M. arvensis* waste biomass for Pb(II) and Co(II) corresponding to different time intervals of 15, 30, 60, 180, 240, and 360 min were investigated, and the results are as shown in Fig. 7. The results regarding the Pb(II) and Co(II) kinetic data revealed that biosorption capacity of *M. arvensis* increased with increase in time. The removal of both Pb(II) and Co(II) ions was rapid in the first 60 min, and equilibrium was established after 240 min. After this time, no significant removal of both ions was observed. The variation in the removal of Pb(II) and Co(II) ions was due to difference in their ionic radii. Ionic radii of Pb (II) and Co(II) are 1.75 and 2.25 Å, respectively. The smaller the cation, the greater is its radius in an aqueous medium. The results showed that biomass biosorption capacity increased with a decrease in hydrated radius of metal ion in aqueous solutions [23]. This biosorption characteristic represented that surface saturation was dependent on the hydrated radius of Pb(II) and Co(II) cations; at a lower hydrated radius of metal ion, biosorption sites took up the available metal more quickly; however, at higher aqueous ionic radius, metal ions need to diffuse to the biomass surface by intraparticle diffusion, and greatly hydrolyzed ions will diffuse at a slower rate.

Kinetic data were fitted using Lagergren pseudo-first-order model and the pseudo-second-order model. The linearized form of first-order Lagergren equation is given as

$$\log(q_e - q) = \log q_e - \frac{k_{1,\text{eds}}}{2.303} t \tag{5}$$

The pseudo-second-order equation is

$$\frac{t}{q} = \frac{1}{k_{2,\text{ads}} \cdot q_e^2} + \frac{1}{q_e} t \tag{6}$$

The obtained kinetic data suggest that the biosorption of Pb(II) and Co(II) ions followed the second kinetic model (Table 2) which relies on the assumption that biosorption may be the rate limiting step [22].

3.8. Effect of temperature

The biosorption of Pb(II) and Co(II) ions was determined at different temperatures keeping all other parameters constant i.e. at optimized condition. Biosorption capacity values of Pb(II) and Co(II) are shown in Fig. 8, at the varying temperature of 30, 40, 50, 60, and 70˚C, respectively. The maximum percentage removal of Pb(II) and Co(II) was obtained at 30˚C which was decreased by further increase in temperature.

Table 2
Comparison between Lagergren pseudo-first-order and pseudo-second-order kinetic models for Pb(II) and Co(II) sorption by *Mentha arvensis* waste biomass (30˚C)

Metals	Pseudo-first-order model			Experimental values	Pseudo-second-order model		
	q_e (mg g)	$K_{1,ads}$ (min^{-1})	R^2	q_e (mg g)	q_e (mg g)	$K_{1,ads}$ (g/mg min)	R^2
Pb(II)	37.70	6.91×10^{-3}	0.977	54.62	75.1	1.09×10^{-3}	0.998
Co(II)	28.70	4.61×10^{-3}	0.857	53.34	76.92	1.61×10^{-3}	1

These results are in accordance with the earlier reported work [16]. The above results show that a slight change in biosorption capacity was observed in case of Pb(II) and Co(II), with biomass decreased rapidly with an increase in temperature. This is because with increase in temperature, the attractive forces between biomass surface and metal ions are weakened and the biosorption decreases. Careful examination of the results revealed that the most of the metal ions were removed at 30˚C.

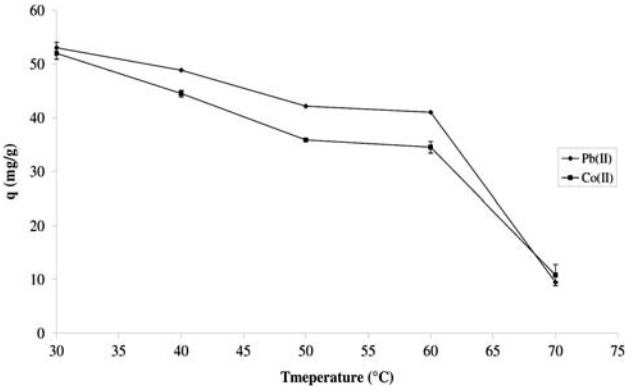

Fig. 8. Effect of temperature on the biosorption of Pb(II) and Co(II) ions from aqueous solutions by *Mentha arvensis* waste biomass.

3.9. Effect of chemical treatments

The effect of different pretreatments on the biosorption capacity of *M. arvensis* waste biomass for the removal of Pb(II) and Co(II) ions is depicted in Fig. 9. The biosorption capacity of *M. arvensis* waste biomass was found in the following order for Pb(II): Triton-X-100 (71.03) > NaOH (68.76) > acetic acid (58.74) > HCl (58.13) > acetone (57.14) > native (53.35). On the other hand, following order for Co(II) ions was observed: HCl (72.16) > Trition X-10 (70.85) > acetic acid (62.79) > acetone (58.79) > NaOH (55.71) > native (51.95). For both the metals Pb(II) and Co(II), acidic pretreatments increased the sorption capacity of the waste biomass of *M. arvensis*. An increase in biosorption of Pb(II) and Co(II) ions as a result of pretreatment could be due to an exposure of active metal binding sites embedded in the cell wall or chemical modifications of the cell wall components [20]. Acids can enhance the uptake capacity of biomass by increasing the surface area and porosity of original sample [17].

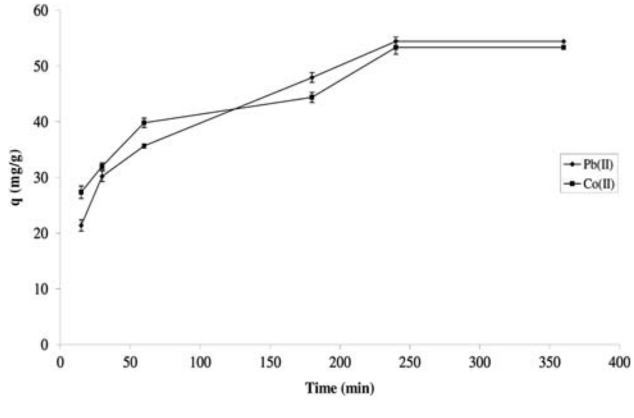

Fig. 7. Effect of contact time biosorption of Pb(II) and Co (II) ions from aqueous solutions by *Mentha arvensis* waste biomass.

Triton X-100 removes oily phase from the cell surface hence sorption capacity was increased. Triton X-100 is a nonionic surfactant. Surfactants are the substances with lyophobic and lyophilic groups capable of adsorbing at interfaces. The adsorption of heavy metals on to biomass from solutions can be enhanced in the presence of surfactants due to reduced surface tension and increasing wetting power.

Alkali treatment can increase the biosorption of heavy metals due to the fact that it may destroy autolytic enzymes causing putrefaction of biomass, removes lipids and proteins that mask binding sites, and could release certain biopolymers from the cell wall that have a high affinity towards heavy metals ions [26].

When the waste biomass of *M. arvensis* was pretreated using bases, the biosorption capacity was increased. For Pb(II) sorption, values of biosorption capacities (mg/g) were observed in following order: sodium hydroxide (68.77) > native (53.05), and order of sorption capacity (mg/g) after basic treatment in case of Co(II) were: NaOH (55.62) > native (51.87) mg/g. A

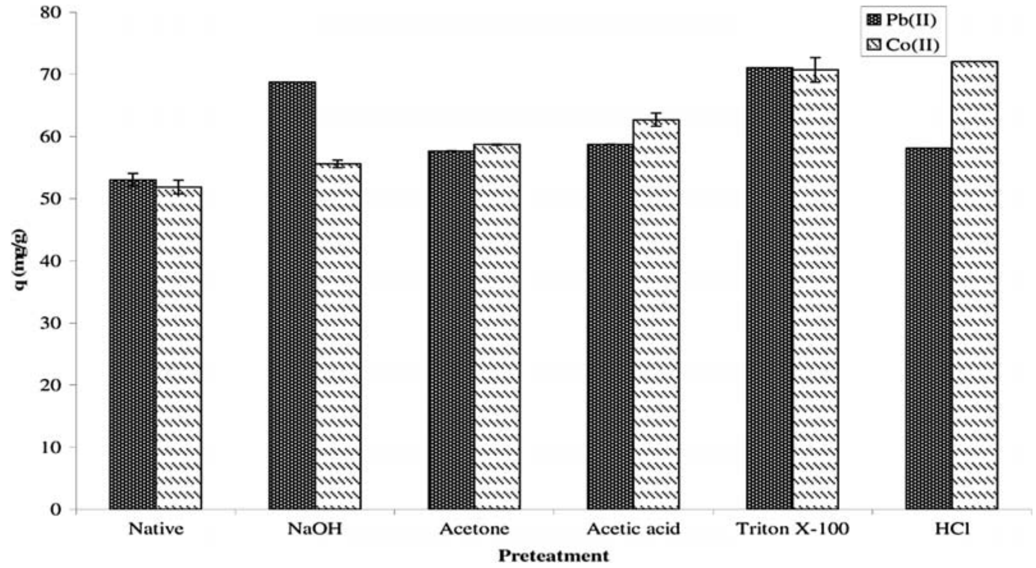

Fig. 9. Effect of chemical treatments on the biosorption of Pb(II) and Co(II) ions from aqueous solutions by *Mentha arvensis* waste biomass.

Table 3
Comparison between *Mentha arvensis* biomass and previously used biosorbents for the removal of Pb(II) and Co(II) from aqueous solutions

Metal	Biosorbents	$q_{\max}$ (mg/g)	Reference
Pb(II)	*Citrus reticulate biomass*	41.16	[20]
	Rose waste biomass	156	[23]
	Cocoa shells	6.2	[27]
	Black gram husk	49.97	[28]
	Ceratophyllum demersum	44.8	[29]
	Myriophyllum spicatum	46.49	[30]
	Brown seaweed *Cystoseira baccata*	186	[31]
	Aspergillus flavus	10.82	[32]
	Baker's yeast	45.87	[33]
	Waste Chinese herb Pang Da Hai	27.1	[34]
	Bacillus sp.	92.27	[35]
	Mentha arvensis biomass	71.03	Present study
Co(II)	*Citrus reticulate biomass*	52.61	[20]
	Rose waste biomass	27.15	[23]
	Activated sludge fed	18.76	[36]
	Sargassum wightii	20.63	[37]
	Green alga Ulva *reticulata*	46.1	[38]
	Oscillatoria angustissima	7.02	[39]
	Mentha arvensis biomass	72.16	Present study

comparison between *M. arvensis* biomass and previously used biosorbents for the removal of Pb(II) and Co(II) from aqueous solutions is given in Table 3.

4. Conclusions

The following conclusions were drawn from the present work.

(1) *M. arvensis* waste biomass has a high affinity for Pb(II) and Co(II) ions from aqueous solutions.
(2) Biosorption capacity of *M. arvensis* biomass varies greatly with initial pH, biosorbent dose, biosorbent particle size, initial metal ion concentration, contact time, etc.
(3) Chemical treatments enhanced the biosorption capacity of biosorbent significantly.
(4) The equilibrium biosorption data agreed well with Langmuir isotherm with high correlation coefficients. The kinetics of the biosorption process was found to follow pseudo-second-order model in batch mode.

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