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Utilization of Extensively Available Environmental Waste *Mentha spicata* for Uptake of Pb(II) from Aqueous Solutions

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The present study was focused on extensively available *Mentha spicata* distillation waste biomass for Pb(II) uptake from aqueous solutions. The biomass was entrapped in alginate bead after adopting a specially carried out process. The effect of various experimental parameters on adsorption of Pb(II) was investigated under laboratory conditions. The results clearly indicated the importance of various experimental parameters such as pH, biosorbent dose, biosorbent particle size, initial metal concentration and contact time for removal of Pb(II) from aqueous solutions. The uptake of Pb(II) by immobilized *Mentha spicata* distillation waste biomass increased with increase in pH reaching a maximum at 5. The equilibrium sorption data agrees well with Freundlich sorption isotherm with high correlation coefficients. The kinetics of the sorption process was found to follow pseudo-second order kinetic model in batch mode and pseudo-first order in continuous mode of adsorption. High Pb(II) uptake capacity of immobilized *Mentha spicata* distillation waste biomass suggested that it could be used as a potential biomaterial to remove Pb(II) ions from aqueous solutions.

Key Words: Pb(II), *Mentha spicata*, Biosorption, Waste biomass, Kinetics.

INTRODUCTION

Inorganic toxicants such as heavy metals can be transferred through the food chain and affect biota directly. Metal toxicity associated with solids in the environment is of particular concern since they can be released into the water column and adversely affect the biota[1]. Heavy metals are not biodegradable and tend to be accumulated in organisms and cause numerous diseases and disorders. Chronic exposure to high amount of lead can result in various and considerable damages to systems of the body, including nervous and reproductive systems and kidneys. Moreover, high blood pressure, anemia, lead poisoning, coma and death can be considered among the most substantial consequences[2]. Lead(II) is particularly a common heavy metal found in wastewater of paint industries. The permissible limit for lead in drinking water is 0.05 mg/L. The permissible limit (mg/dm^3) for Pb(II) ion in wastewater, given by the Environmental Protection Agency, is 0.05 mg dm^{-3} and that of the Indian standards institution (BIS) is 0.1 mg/dm^3. The presence of heavy metal ions at concentrations above critical values in the environment is unacceptable and their removal from the wastewater is very important[3,4].

The search for new technologies involving the removal of toxic metals from wastewaters has directed attention to biosorption, based on metal binding capacities of various biological materials. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency, minimization of chemical and biological sludge, no additional nutrient requirement, regeneration of biosorbent and possibility of metal recovery[5]. Although abundant natural materials of cellulosic nature have been suggested as biosorbents and less work has been done in that respect[5]. The removal of heavy metal ions by biosorption using biological materials have been widely studied in the last decade due to its potential, particularly in wastewater treatment. In addition to all these a variety of plant waste biomasses have been used as biosorbents for Pb^{2+} including neem leaves, sugar cane, *Sphagnum* moss, seaweed, sunflower waste, maize, *Rhizophora mangle* and cotton *etc*. The sorption of metals by this kind of material might be due to the presence of carboxyl, hydroxyl, sulphate, phosphate and amino groups that can bind metal ions[6]. *Mentha spicata* common names are mint, brown mint, garden mint, lamb mint, mackerel mint, Lady's mint, sage of Bethlehem. *Mentha spicata* (Spear Mint or Spearmint) is a species of mint native to much of Europe and southwest Asia, though its exact natural range is uncertain due to extensive early cultivation. It belongs to kingdom : plantae, order: Lamiales, family: Lamiaceae and genus : Mentha. *Mentha spicata* is distilled to extract essential oil for food and medical industries. The plant biomass left after extraction of essential oil is a waste material without any commercial importance. The present study explores the utilization of distillation waste of *Mentha Spicata* available in abundance as a potential biosorbent for Pb(II) from aqueous streams.

EXPERIMENTAL

Mentha spicata distillation waste biomass was obtained from Rosa Laboratory, Institute of Horticultural Sciences, University of Agriculture, Faisalabad, Pakistan. The obtained biomass was oven dried at 70 ºC for 3 days. The dried biomass was grinded into powder form using a food blender. The powder biomass was sieved into different mesh sizes (*i.e.* > 0.250, 0.250-0.355, 0.355-0.500, 0.500-0.710 and 0.710-1 mm) using Octagon siever. The sieved biosorbent was stored separately in sealed bottles to prevent re-adsorption of moisture[7].

Immobilization of biomass: One gram of biosorbent powder and 2 g of sodium alginate were added in 100 mL of distilled water. This suspension was mixed at high speed in a food blender. The solution was heated at 70 ºC to obtain a thick solution. Afterwards this solution was taken in a burette and introduced in a drop wise manner into 0.1 M $CaCl_2$ solution taken in a conical flask. The formed beads were found to have a uniform size of approximately 0.350 mm.

Stock solution of lead(II): The stock solution of lead(II) was prepared by dissolving 1.59 g of lead nitrate in 1000 mL of deionized water. The solutions of desired concentrations were prepared from the stock solution.

Biosorption studies: In all the experiments, 100 mL lead(II) solution of known concentration was taken in 250 mL conical flask along with a control for each experiment. Weighed dose of biosorbent was added to each conical flask. Conical flasks were sealed with aluminium foil. The experiments were conducted in triplicate for concordant readings. Samples were filtered after 24 h using Whatman filter paper No. 40 and stored in plastic sample bottles. The lead(II) concentration was determined after diluting the solution into 5-10 mg/L by atomic absorption spectrophotometer.

Batch biosorption experiments: Different experimental parameters were measured to determine the optimum sorption of Pb(II) by immobilized *Mentha spicata*. The following parameters were included in the present study.

Effect of pH: Effect of pH on adsorption of Pb(II) was determined at various pH values ranging from 2.5 to 5.

Biosorbent dose: To study the effect of biosorbent dose on biosorption of Pb(II) various doses of optimized biosorbent size (0.05, 0.1, 0.2, 0.3, 0.4, 0.5 g) were selected and applied to 100 mL of 100 mg/L Pb(II) solution having pH 5.

Biosorbent size: To study the effect of biosorbent particle size, *Mentha spicata* was graded into five different sizes *i.e.* < 0.250, 0.250-0.355, 0.355-0.500, 0.500-0.710 and 0.710-1 mm. To 100 mL of 100 mg/L lead(II) solution having pH 5, 0.1 g of biomass of varied size was applied to study the effect biosorbent particle size.

Initial metal concentration: The effect of initial metal concentrations was studied at five different concentration *viz*. 25, 50, 150, 200 and 400 mg/L at 0.1 g biomass dose, < 0.250 mm particle size and pH 5.

Contact time: The effect of contact time was studied at five different time intervals *viz*. 25, 15, 30, 60, 120, 180, 360, 720, 1440 min at 0.1 g biomass dose, < 0.250 mm particle size, 100 mg/L initial metal concentration and pH 5. Whenever needed the solution pH was maintained using 0.1 M solutions of HCl and NaOH. At end of each experiment the solutions were filtered using Whatman filter paper No. 40 ashless.

Effect of pretreatment on biomass

Physical pretreatments: In physical pretreatments, the immobilized biomass was physically modified by heating (1.25 g of beads) in an electric oven for 0.5 h. For boiling pretreatment 1.25 g of beads taken in 100 mL distilled water were boiled for 0.5 h in a glass beaker on a flame.

Chemical pretreatments: The waste biomass (1.25 g) was pretreated by soaking for 24 h in 100 mL of 0.1 N solutions of various organic and inorganic reagents: HCl, H_2SO_4, NaOH, $Ca(OH)_2$, CH_3COCH_3, C_2H_5OH. Pretreated immobilized beads were filtered out and washed extensively using distilled water before the experiments.

Metal uptake: The uptake of Pb(II) was calculated by the metal concentration method[8]. The metal uptake (q_e) and % removal was calculated from the mass balance and % age removal equations (1) as follows:

$$q_e = V (C_i-C_e)/1000 W \quad (1)$$

where, C_i = initial metal concentration (mg/L); C_e = Final concentration (mg/L); V = volume of the solution; W = Mass of biosorbent in g.

The extent of sorption in % is calculated from the relation[9].

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

Statistical analysis: All results are discussed by calculating mean ± standard deviation values. All statistical analysis was done using Microsoft Excel 2003, version office XP. The correlation coefficient (R^2) values of the linear form of Langmuir isotherm, Freunlich isotherm, pseudo-first order and pseudo-second order kinetic models were also determined using statistical functions of Microsoft Excel, 2003.

RESULTS AND DISCUSSION

Effect of pH: The effect of pH on Pb(II) uptake by immobilized *Mentha spicata* distillation waste biomass (IMSDWB) at fixed dose of 0.1 g, initial metal concentration of 100 mg/L and contact time of 24 h is shown in Fig. 1. The pH ranges from 2 to 5 but maximum Pb(II) removal both for native and immobilized biomass was observed at 5 pH. When pH further increased, the soluble lead precipitated from the solutions. The effect of pH on metal biosorption has been studied by many researchers and the results indicated that pH of solution can significantly influence biosorption[10,11]. With increase in pH the functional groups on the cell wall with negative charge increases due to deprotonation of the metal binding sites, which promotes the metal uptake[12,13] also observed maximum Pb(II) removal at pH 5 with untreated and treated rose waste biosorbent. It was reported that at highly acidic pH (<3) Pb(II) ions compete with H^+ on binding sites of cells and adsorption is lowered. However, at higher pH (> 5) solubility of Pb(II) was lowered due to insoluble precipitation[14,15].

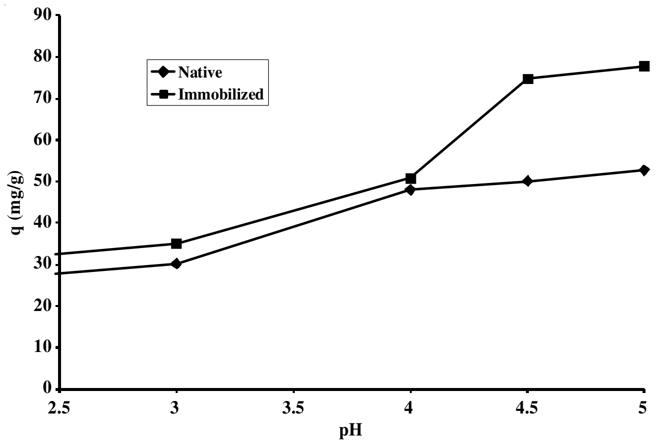

Fig. 1. Effect of pH on biosorption of Pb(II) by immobilized *Mentha spicata* distillation waste biomass

Effect of biosorbent dose: Biomass concentration strongly affects the amount of lead(II) removal from aqueous solutions. By increasing the mass of immobilized *Mentha spicata* distillation waste biomass. Its biosorption capacity, q was noticed to be reduced both for the native and the immobilized case. The experiment was conducted at pH 5 and initial metal concentration of 100 mg/L. Biosorbent dose has great influence on the removal of Pb(II). Results showed the maximum Pb(II) removal at 0.05 g (120.10 mg/g) for native (Fig. 2) and at 0.05 g (160.21 mg/g) for immobilized *Mentha spicata* distillation waste biomass (Fig. 2). The removal of Pb(II) depends on the quantity of biomass dose used. Biosorbent materials contain weak acidic and basic functional groups. The binding of heavy metal cations is determined primarily by the state of dissociation of week acidic groups[16]. Higher uptake of Pb(II) at low biosorbent dose may be due to increased metal-to-sorbent ratio[16]. As the biomass dose increased the biosorption quantity per gram of dose decreased. The reason is that the amount of lead ions was changeless in the system. The more the biosorbent dose used the little the biosorptive quantity adsorbed per gram of dose[17]. The similar effect was reported by Quek *et al.*[18] for sago waste for the sorption of lead and copper.

Effect of biosorbent size: There was rapid removal of Pb(II) by beads of immobilized *Mentha spicata* distillation waste biomass made from smaller particles. The experiment was conducted with biosorbent size ranging from 0.250 to 1 mm at pH 5 and initial metal concentration of 100 mg/L. Biosorbent size has a great influence on the removal of Pb(II). The maximum Pb(II) removal was noted at particle size of 0.250 mm for both native (52.55 %) and immobilized *Mentha spicata* distillation waste biomass (77.3 %) (Fig. 3). This is generally because of the increase in the total surface area which

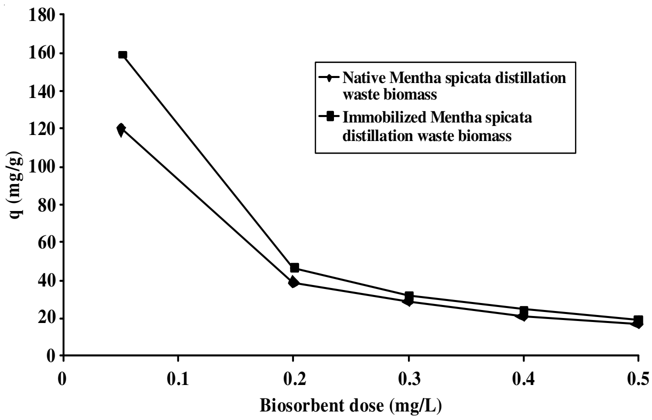

Fig. 2. Effect of immobilized *Mentha spicata* dose on biosorption of Pb(II)

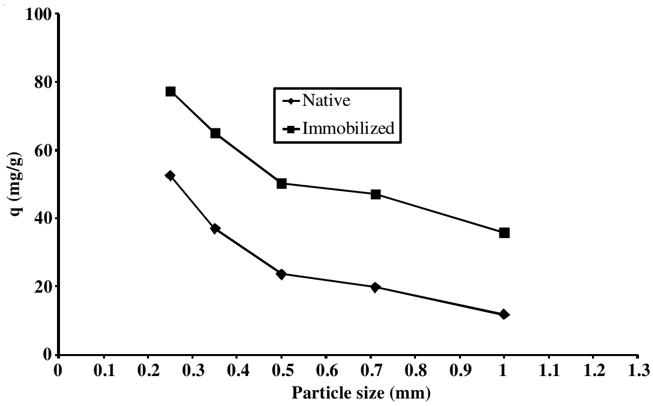

Fig. 3. Effect of biosorbent size of immobilized *Mentha spicata* distillation waste biomass on biosorption of Pb(II)

provided more sorption sites for the metal ions. By using smaller particles, the increased removal of sorbate has been noted during a study into the removal of colour by silica[12,19].

Effect of pretreatment: The effect of pretreatment on uptake capacity of *Mentha spicata* distillation waste biomass is shown in Fig. 4. The metal sorption capacity (mg/g) of physically treated *Mentha spicata* (native) was found to be in the order heated (80.4) > boiled (80) > native (47.45) and the metal sorption capacity (mg/g) of physically treated immobilized *Mentha spicata* distillation waste biomass was found to be in the order heated (81.6), boiled (79.8), immobilized (78). Heating and boiling created more sorption sited on the biomass surface[20]. It was reported earlier that NaOH can destroy autolytic enzymes because putrefaction of biomass and remove proteins and lipids that mask the reactive sites [21,22]. In the present study, pretreatment with NaOH totally damaged beads of immobilized *Mentha spicata* distillation waste biomass. Biosorption capacity (mg/g) of native *Mentha spicata* was: methanol (72.4) > acetone (70.2) > ethanol (66.9) > HCl (65.4) > H_2SO_4 (59.2) and immobilized *Mentha spicata* distillation waste biomass was methanol (83.8) > ethanol (82.2) > acetone (80.1) > HCl (69) > H_2SO_4 (62.2) (Fig. 4). An increase in biosorption of Pb(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 cell wall components[9, 23].

Effect of contact time: The contact time plays an important role in the biosorption of Pb(II).The effect contact time was

TABLE-1
COMPARISON BETWEEN LAGERGREN PSEUDO- FIRST ORDER AND PSEUDO- SECOND ORDER KINETIC MODELS FOR Pb(II) BY IMMOBILIZED *Mentha spicata* DISTILLATION WASTE BIOMASS

Pseudo-first order kinetic model				Experimental value	Pseudo-second order kinetic model		
Biomass	q_e (mg/g)	$K_{1,ads}$ (min^{-1})	R^2		q_e (mg/g)	$K_{2,ads}$ ($g.mg^{-1}.min^{-1}$)	R^2
Native	18.80	2.99×10^{-2}	0.603	53.00	55.86	3.20×10^{-4}	0.999
IMSDWB	26.24	6.44×10^{-3}	0.598	78.90	82.65	4.45×10^{-5}	0.998

IMSDWB = Immobilized *Mentha spicata* distillation waste biomass.

TABLE-2
COMPARISON BETWEEN LANGUMIR AND FRANDLICH ISOTHERM PARAMETER

Langumir Isotherm Parameters				Experimental value	Frendlich isotherm parameter			
Biomass	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
Native	204.08	5.88×10^{-5}	0.999	205.00	157.76	1.67	0.862	0.948
IMSDWB	188.68	6.36×10^{-4}	0.998	187.98	216.18	5.15	0.698	0.878

IMSDWB = Immobilized *Mentha spicata* distillation waste biomass.

studied at pH 5, biosorbent dose 0.1 g and metal concentration 100 mg/L. Samples were collected at regular intervals and analyzed for Pb(II) ion concentration after filtration (Fig. 5). The equilibrium was attained after 6 h and the maximum percentage removal observed was 52.76 % and 78.8 % for native and immobilized *Mentha spicata* distillation waste biomass respectively. After the equilibrium was achieved, the amount of adsorbed Pb(II) ions did not change significantly with time. For economical waste water treatment system, equilibrium is an important parameter[20]. Various steps are involved in the transfer from bulk solution to binding sites[24].

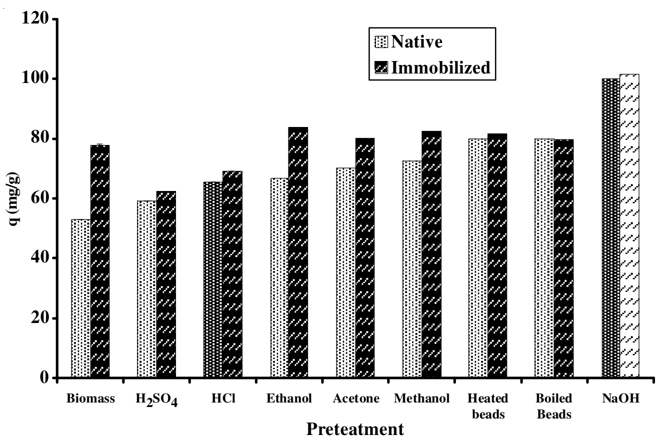

Fig. 4. Effect of pretreatment of *Mentha spicata* distillation waste biomass on Pb(II) biosorption

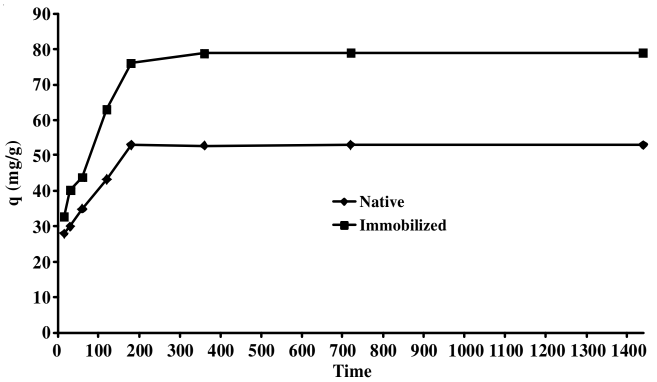

Fig. 5. Effect of time on biosorption of Pb(II) by immobilized *Mentha spicata* waste biomass

Pseudo-first order[25] and pseudo-second order[26] kinetic models were applied to sorption data of Pb(II) and best fit was observed for later model (Table-1). A comparison between kinetic models suggested the coefficient of correlation (R^2) for the pseudo-second order is higher in comparison to pseudo-first order. Experimental q_e (mg/g) suggested that model fitted to the data was pseudo-second order kinetic model which indicated that the metal biosorption process is dependent on the number of metal ions present in the solution as well as the free biosorption sites on the biosorbent surface[16].

Effect of initial metal ion concentration: The Pb(II) uptake by using *Mentha spicata* distillation waste biomass (native and immobilized) corresponding at different concentrations (25, 50, 150, 200 and 400 mg/L). The results showed that sorption capacity of *Mentha spicata* distillation waste biomass increased with increase in initial metal ion concentration of Pb(II). The maximum Pb(II) uptake (mg/g) was observed at 400 mg/L. This sorption characteristic indicated that surface saturation was dependent on the initial metal concentrations[9,27] during the study of metal ion sorption found the concentration is an important factor[27].

To determine the relationship between sorption capacity (q) and aqueous concentrations (C_e) at equilibrium, sorption isotherm models are widely employed for fitting the data, of which the Langmuir and Freundlich equations are widely used. Modeling the equilibrium data is very important for the industrial application of biosorption since it can be employed to compare the efficacy of different biomaterials under different operational conditions, designing and optimizing operating procedures[28]. The results indicated that the model better fitted to the data was Langmuir model (Table-2) which indicated that adsorption occurred on heterogeneous surface. Similar results were earlier reported[16].

Effect of column study: For practical applications, it was necessary to determine the maximum Pb(II) uptake in column set up. The conditions required for this experiment were pH 5, initial metal concentration 100 mg/L, biosorbent dose 0.5 g and time 5, 10, 20, 30, 60, 120 and 240 min. The results indicated that the maximum Pb(II) uptake was found at 240 min.

Desorption experiments: Immobilized *Mentha spicata* distillation waste biomass beads after adsorption of Pb(II) in column study were treated with 0.1N solutions of NaOH, HCl and EDTA (Fig. 6). Maximum desorption of Pb(II) from native

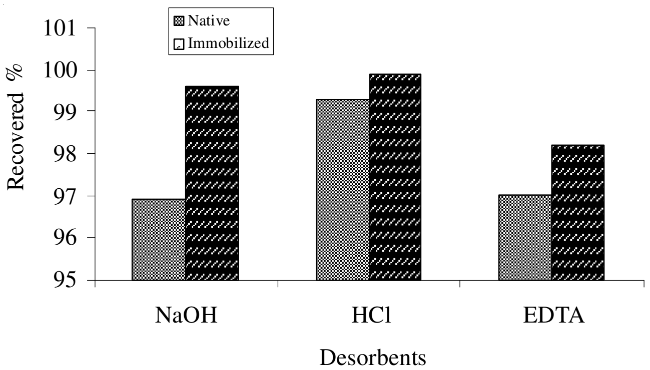

Fig. 6. Percentage recovery of adsorbed Pb(II) from *Mentha spicata* distillation waste biomass

biomass was obtained using 0.1 N HCl solution (99.30 %). Desorption using EDTA and NaOH was 97.01 % and 96.91 %, respectively. Pb(II) desorption from immobilized *Mentha spicata* distillation waste biomass using various reagents was as follows: HCl (99.90 %), NaOH (99.60 %) and EDTA (98.20 %).

Conclusion

The present study illustrated the effect of various experimental parameters such as pH, dose, contact time, initial Pb(II) concentration, column study, pretreatment and desorption on Pb(II) uptake using native and immobilized *Mentha spicata* distillation waste biomass.

Langmuir adsorption isotherm model was fitted well to Pb(II) adsorption data.

Contact time data of Pb(II) adsorption by native and immobilized *Mentha spicata* distillation waste biomass fitted well to pseudo-second order kinetic model in batch mode and pseudo-first order kinetic model in continuous mode. High Pb(II) uptake capacity suggested that immobilized *Mentha spicata* distillation waste biomass can be used as a potential biosorbent.

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