Biosorption of Pb (II) by Local Gram (*Cicer arietinum*) Cultivar Biomass

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Summary: Biosorption of heavy metals can be an effective process for the removal and recovery of heavy metal ions from aqueous solutions. In this paper, the comparative adsorption properties of non-treated and basically pre-treated pods biomass of local gram cultivar (LGC) biomass with NaOH, $Ca(OH)_2$ and $Al(OH)_3$ for Pb (II) uptake was investigated. Equilibrium isotherms and kinetics results were obtained from batch adsorption experiments. The biosorption capacities were solution pH dependent and the maximum capacity obtained was 34.28 mg/ g at a solution pH of about 5. The biosorption kinetics was found to be fast, with most of adsorption within 240 min and equilibrium reached at 480 min. This study demonstrated that the NaOH pre-treated pods biomass of LGC could be used as an effective biosorbent for the treatment of Pb (II) containing wastewater streams.

Introduction

Natural freshwaters, i.e. surface and ground waters are the ultimate recipients of the most toxic substances generated by industrial, agricultural, and domestic activities [1]. Heavy metals are discharged from various industries such as electroplating, metal finishing, textile, storage batteries, mining, ceramic and glass. Pb (II) is the common contaminant of wastewater from these industries. As it pose serious environmental problems that are dangerous to human health, considerable attention has been given to the methods for its removal from industrial wastewaters [2-3]. The traditional approaches for removing or recovering Pb (II), such as precipitation, oxidation/ reduction, ion exchange, filtration, electrochemical processes, membrane separations, and evaporation, all exhibit several disadvantages, such as high cost, incomplete removal, low selectivity, high energy consumption, and generation of toxic slurries that are difficult to be eliminated [4-6]. Biosorption of heavy metals from aqueous solutions is a relatively suitable technology for the treatment of wastewater [7]. Adsorbent materials (biosorbents), derived from a suitable biomass, can be used for the effective removal and recovery of heavy metallic ions from wastewater streams. The major advantages of biosorption over conventional treatment methods include: low cost, high efficiency of metal removal from dilute solutions, minimization of chemical and or biological sludge, no additional nutrient requirements, regeneration of biosorbent, and possibility of metal recovery [8].

It is desirable to search for alternative, low cost and naturally occurring biodegradable adsorbents having good adsorbent properties and low value to inhabitants. A range of products has been examined, including pillared clay [9], Chitin [10], *Thiobacillus ferrooxidans* [4], Cork [6], Sago waste [11], banana pith [12], peanut skins [13], Bone char [14], *Medicago sativa* (Alfalfa) [15], Mycelial dead biomasses (*Rizopus arrhizus, Mucor miehei* and *Pencillium chrysogenum*) [16], Spagnum Moss Peat. [17], *Cassia fistula* (Golden shower)[18] and *Moringa oleifera* Lam. (horseradish tree) biomass [19], just to mention a few. The up to dated detailed studies on the effects of basic pretreatment of biomass yet have not been widely conducted. In this regard the present study was planned to find the biosorption ability of the local gram cultivar pods biomass pretreated with bases, to bind Pb (II) from aqueous solutions in comparison to native biomass. The uptake capacities of non treated and basically pretreated

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LGC pods biomass for Pb (II) ions in aqueous solutions were evaluated from equilibrium isotherms.

Results and Discussion

Effect of pH

The solubility of metal ions and concentration of the counter ions on the functional groups of the biomass cell walls is strongly dependent on solution pH which makes it an important parameter on biosorption of metal ions from aqueous solutions. The equilibrium metal uptake of LGC biomass from 50 mg/ L Pb (II) solutions at various controlled pH values are presented in Fig. 1. The uptake of Pb (II) increases with an increase in solution pH. The uptake capacity increased from 17.3 mg/ L at pH 1 to 34.28 mg/ L at pH 5. At lower pH (1-3) values, Pb (II) removal was partially inhibited, as a result of the competition between hydrogen and Pb (II) ions on the sorption sites, with an apparent preponderance of hydrogen ions, which restricts the approach of metal cations as in consequence of the repulsive force. At higher pH values 4-5, there are lower numbers of competing hydrogen ions and more ligands are exposed with negative charges, resulting in greater Pb (II) sorption. Whereas at pH higher than 5, Pb $(NO_3)_2$ hydrolyzes into insoluble $Pb(OH)_2$,which starts precipitating from solutions at higher pH values, making true sorption studies impossible, similar results have been reported for metal biosorption studies in literature [20-28].
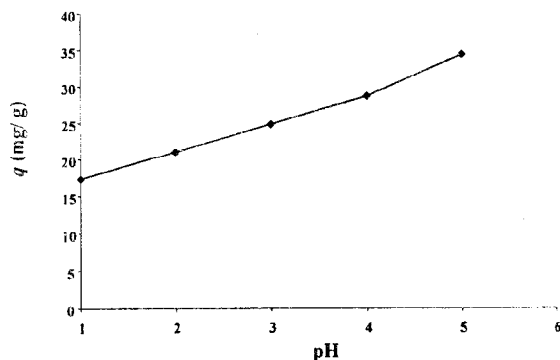
Effect of Biosorbent Dose

Increasing the mass of differently pretreated LGC biomass caused the sorptive capacity, q, to be reduced (Fig. 2). The results demonstrated that the biomass concentration strongly affected the amount of metal removed from aqueous solutions. Moreover, as the biomass concentration rises, the maximum biosorption capacity drops, indicating poorer biomass utilization (lower efficiency). Biosorbent dose seemed to have a great influence in biosorption process. Dose of biomass added into the solution determine the number of binding sites available for adsorption. The decrease in sorption capacity with increasing biomass dose suggests that at constant concentration on increasing sorbent amount, the number of binding sites increase but number of Pb (II) ions in solution remained same which reduced the sorption capacity [18-29].
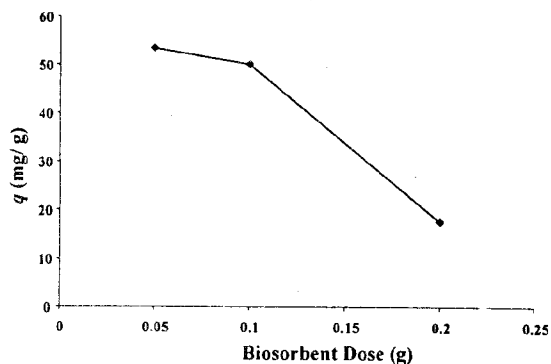

Fig. 2.   Effect of amount of sorbent on the biosorption of Pb (II) by LGC biomass.

Effect of Particle Size of Biosorbent

The effect of altering the sorbents particle size on the sorption capacity, q (mg/ g) showed that, there was a more dominant removal of Pb (II) by the smaller particles (< 0.255 mm) (Fig. 3). This was most probably due to the increase in the total surface area which provided more sorption sites for the metal ions. This was not the case with the sorption of Pb (II) for the larger particle size (0.255 mm to 0.355 mm) [18-30].

Pretreatment Effect on Pb (II) Uptake

The uptake of Pb (II) by the LGC biomass pretreated differently is shown in Fig.4. Native

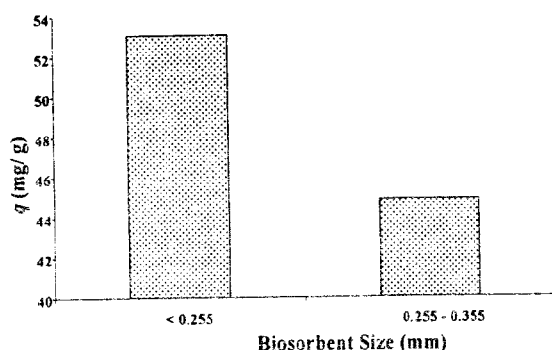Fig. 1.   Effect of pH on the biosorption of Pb (II) by LGC biomass.

Fig. 3. Effect of two different sorbent particle sizes on biosorption of Pb (II) by LGC biomass.
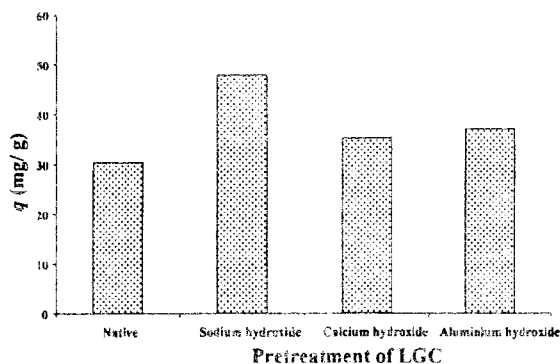

Fig. 4. Comparison of native and treated LGC biomass for the removal of Pb (II) from aqueous solutions.

biomass (untreated biomass) washed with water only was used as a control. Pods pretreated with NaOH exhibited the maximum rate of adsorption. Pretreatment of microbial biomass or other agricultural biomass with alkali has been shown earlier to enhance their metal biosorption capacities [31]. As NaOH is a more stronger base, because it is more ionsable than $Ca(OH)_2$ and $Al(OH)_3$, this effect was prominent with this base. Removal of surface impurities, destruction of autolytic enzymes, rupture of cell-membrane and exposure of available binding sites for metal bioadsorption after pretreatment might be the reason for the increase in metal biosorption. Because biomass pretreated with NaOH exhibited better metal uptake capacities, therefore it was used in all the further studies.

Effect of Initial Metal Concentration

The results revealed that metal removal increased with increase in initial concentrations from 50 to 200 mg/ L (Fig.5). Effect of Pb (II) concentration between 50-200 mg/ L was analyzed because most often Pb (II) concentration in industrial effluents was in the said range. These observations can be explained by the fact when metal ion concentrations are increased, binding sites become more quickly saturated as the amount of biomass concentration remained constant [32].
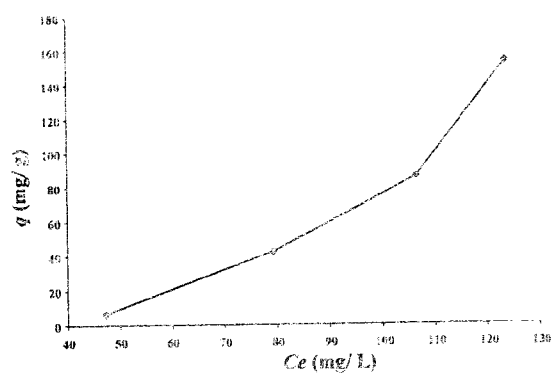

Fig. 5. Effect of different initial metal concentrations on biosorption of Pb (II) by pretreated (NaOH) LGC biomass

Adsorption Isotherms

In order to study the adsorption mechanism/dynamics, Langmuir and Freundlich isotherms (Fig. 6 and Fig. 7) respectively were used to represent the equilibrium relationship for different initial Pb (II) concentrations experiment. Langmuir equation transforms to the linearized form (2.6.1):

$$\frac{C_e}{q_e} = \frac{1}{q_{max}k_L} + \frac{C_e}{q_{max}} \quad\text{------------ (2.6.1)}$$

Where q_e is metal ion sorbed (mg/ g), C_e is the equilibrium concentration of metal ion solution, q_{max} and K_L are the Langmuir constants. The Langmuir equation assumes that surface of the biosorbent consist of adsorption sites, all adsorbed species interact with only a site and not with each other and adsorption is limited to monolayer. It is
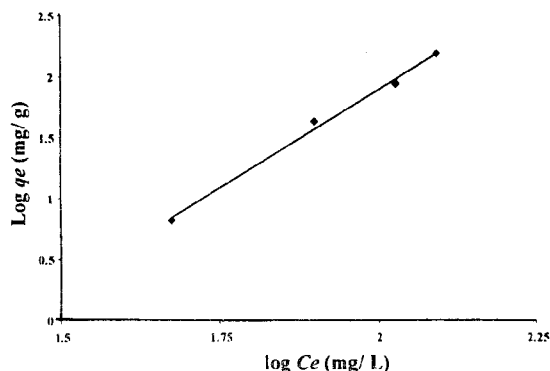
Fig. 6.   Freundlich plot for biosorption of Pb (II) by LGC biomass modified with NaOH.
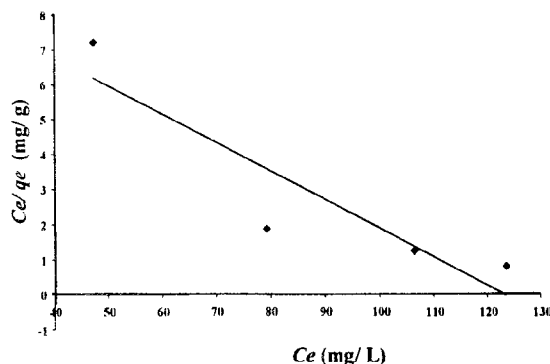

Fig. 7.   Langmuir isotherm for biosorption of Pb (II) by LGC biomass modified with NaOH.

then assumed that once a metal ion occupies a site, no further sorption can take place. The Freundlich equation is an empirical relationship describing the adsorption of the solutes from a liquid to solid surface. Linearized form of Freundlich equation is (2.6.2):

$$log \ q_e = \frac{1}{n} log \ C_e + log \ k \ \text{---------------- (2.6.2)}$$

Where q_e is metal ion sorbed (mg/ g), C_e is the equilibrium concentration of metal ion solution, mg/ L, K and $1/ n$ are Freundlich constants. The Freundlich (Fig.6) model (q = 152.79 mg/ g, K = 2.76 × 10^{-5} mg/ g, R^2 = 0.9939) better represented the sorption process, in comparison to the model of Langmuir (q = 35.71 mg/ g, K = 35.71 × 10^{-3} mg/ g, R^2 = 0.2093) (Fig.7) as represented by model parameters.

Biosorption Kinetics of Pb (II)

A kinetic study with different time intervals having fixed metal concentration, biosorbent amount and biosorbent particle size was performed. Time required for attaining equilibrium was 480 min, under the studied conditions (Fig. 8). The rate of metal uptake is influenced by factors affecting mass transfer from bulk solution to binding sites. From the obtained results it was indicated that various steps are involved in the transfer of metal from bulk solution to binding sites [33]. First is the bulk transport of metal ions in solution phase, which is usually rapid because of mixing and flow [34]. Second, film transport involves diffusion of metal through a hydrodynamic boundary layer around the biosorbent surface, and third, actual adsorption of metal ions by active sites of the biomass which is considered to be rapid and equivalent to an equilibrium reaction [33-36].
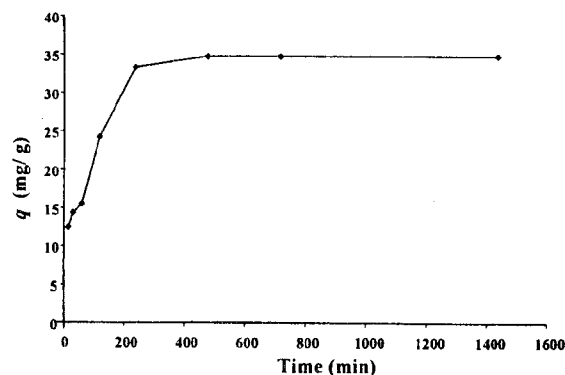

Fig. 8.   Effect of sorption time on the uptake of Pb (II) from aqueous solutions by treated biomass.

Kinetic Modeling

Two different kinetic models (pseudo first and second order models) were used to adjust the experimental data of Pb (II) biosorption on NaOH pretreated LGC biomass [10, 17]. The linear form pseudo first order Lagergren model (Fig. 9) is generally expressed as (2.8.1):

$$log(q_e - q) = log \ q_e - \frac{k_{1,ads} \ t}{2.303} \ \text{------------- (2.8.1)}$$
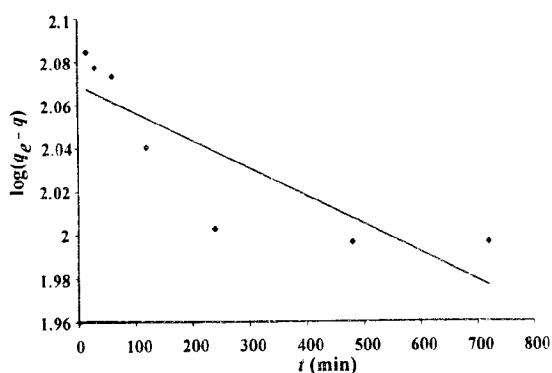
Fig. 9. Plot of Lagergren model for first order sorption kinetics of Pb (II) onto basically (NaOH) treated LGC biomass.

Where q_e and q are the amounts of adsorbed metal ions on the biosorbent at the equilibrium and at any time t, respectively; and $k_{1,ads}$ is the Lagergren rate constant of the first-order biosorption. The coefficient of correlation (R^2) for the first order kinetic model was 0.736. The pseudo second order model is based on the assumption that biosorption follows a second order mechanism. Linear form of pseudo second order model (Fig. 10) can be expressed as follows (2.8.2):

$$\frac{t}{q} = \frac{1}{k_{2,ads}\, q_e^2} + \frac{t}{q_e} \quad\text{----------------------} \quad (2.8.2)$$
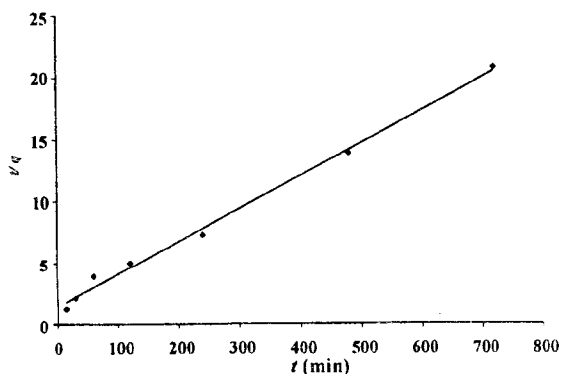

Fig. 10. Plot of pseudo second order kinetic model for Pb (II) uptake by basically (NaOH) treated LGC biomass.

Where $k_{2,ads}$ is the rate constant of second order biosorption (g/ mg. min). q_e is the mass of

metal adsorbed at equilibrium (mg/ g), q_t the mass of metal at time t (min). The coefficient of correlation for the second order kinetic model (R^2 = 0.9981) was approximately equal to 1 and the estimated value of q_e (q_e 36.10 mg/ g, $k_{2,ads}$ 6.51 × 10^{-4} g/ mg. min) also agreed with the experimental one (36.10 mg/ g). Both facts suggest that the sorption of Pb (II) follows the second-order kinetic model, which is based on the assumption that biosorption may be the rate limiting step in comparison to pseudo first order Lagergren model (q_e = 117. 27 mg/ g, $k_1 ads$ = 4.34 × 10^{-5}, R^2 = 0.736).

Experimental

Materials

Samples of the LGC biomass were collected from main vegetable market of Faisalabad, Pakistan. The collected biomass was extensively washed with deionized water and dried at 60 °C under atmospheric pressure for 72 h. All the dry samples were ground to obtain powder of uniform size.

Pretreatment of Biomass

The Pb (II) uptake capacity was tested using basic treatment of LGC biomass. For this purpose, finely ground biomass was soaked in excess of 0.1N solution of each of NaOH, Ca (OH)₂ and Al (OH)₃ for 24 hours (1: 25). The contact time of 24 h was selected to provide sufficient time for interaction. The suspensions were filtered thoroughly and washed extensively with deionized water until a pH 7 ± 0.1 was obtained and then air dried. The biomass was further oven dried at 60 °C for 72 h till constant weight. The dried samples were ground and passed through laboratory vibro-sieving machine prior to their testing for metal biosorption. The fraction of particles between < 0.255 mm and 0.255 - 0.355 mm was used in all the experiments.

Reagents

Analytical grade reagents including Pb (NO₃)₂, Conc. HNO₃, NaOH, Ca(OH)₂, Al(OH)₃ and Pb (II) atomic absorption spectrometry standard solution were used through out the study. All chemicals were purchased from Fluka Chemicals.

Batch Uptake Experiments

Pb (II) uptake potential of LGC biomass was tested by contacting 0.05, 0.1 and 0.2g (dry weight) of biomass size < 0.255 mm and 0.255-0.355 mm at pH 3, 4 and 5 with 100 mL of metal solutions of known concentrations (50, 100, 150 and 200mg/ L) at temperature 30 °C (maintained) and 100 rpm for 24 h. To check the influence of contact time on sorption process and to determine the sorption equilibrium point, the samples at various time intervals ranging from 15 to 1440 min were analyzed during study. The biomass was removed by filtration through a 0.45 μm membrane filter (Millipore), and the filtrates were analyzed for metal concentrations by atomic absorption spectrophotometery using a Perkin-Elmer AAnalyst 300 atomic absorption spectrometer equipped with an air-acetylene burner and controlled by Intel personal computer. Whenever pH control was required, solution pH was adjusted to required value using 0.1 N HNO_3 or 0.1 N NaOH solutions towards the equilibrium. The experiments beyond pH 5 were not conducted due to precipitation of metal hydroxide from solutions which made true sorption studies impossible. The Pb (II) uptake was calculated by the simple concentration difference method [35]. The initial concentration C_o (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 equation (3.4.1) as follows [37]:

$$qe = \frac{V\,(Ci - Ce)}{W} \text{ ------------------------ (3.4.1)}$$

'Where V is the volume of the solution in mL and W is the mass of the sorbent in g.

Conclusions

The major findings in this study were, this work illustrated an alternative solution for the management of the unwanted biological material LGC. The obtained results suggested that LGC could be utilized as a biosorbent for the removal of Pb (II) from wastewater.

Basic pretreatment of LGC was resulted in enhancement of sorption capacity of biosorbent. The sorption isotherms followed the Freundlich type mechanism suggesting heterogeneous sorption

character. The sorption of Pb (II) ions rapidly occurred in first 15 min followed by slow adsorption till equilibrium reached at 480 min. The process was well described by Lagergren model for second order sorption kinetics.

Acknowledgment

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