

REMOVAL OF HEAVY METAL LEAD (PB) (II) BY BIOSORPTION PROCESS USING PAPER SHELL MUSSEL (*ANODONTOIDES FERUSSACIANUS*)Suleman Shahzad^{1*}, Noman Shahzad³, Atif Yaqub¹, Umair Sadiq¹, Usman Ahmad² and Mudassar Hussain¹¹Department of Zoology, GC University, Lahore, Pakistan.²Department of Biotechnology, Punjab University, Lahore, Pakistan.³Department of Biotechnology, South Asian University, New Delhi, India.***Corresponding Author: Suleman Shahzad**

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ABSTRACT

The understanding is on the rise that accumulations of heavy metal pollutants in the environment, being added by industrial effluents, have altered geochemistry of water and soil as well as adversely affected the inhabiting fauna and flora. Simultaneously emerged has urgent need to develop effective technologies to reduce load of these hazardous wastes from the environment. Recently, biosorption has come up as effective tool in which biomass of various organisms have been tested. In the present study, the biosorptive potential of shell biomass of cylindrical paper shell mussel (*Anodontoides ferussacianus*) has been investigated for removal of toxic heavy metals, such as Pb (II) ions. Maximum removal was found to be 200 mg/L for both Pb (II). Various physico-chemical factors have been optimized for biosorptive capacities of sorbates by sorbents. Optimum pH was found to be 6 and optimum temperature was 30°C for Pb (II). Optimum and biomass concentration was 15 mg/L in case of the metal ions. Various adsorption models were elucidated to data, such as Langmuir, Freundlich and Temkin isotherms whereas Freundlich model was found to be fittest showing multilayer sorption. Pseudo-second order kinetic model was also found to fit for this study with regression coefficient value of 0.99. Additionally, Fourier Transform Infra-red Spectroscopic studies (FTIR) indicated various electronegative functional groups on the surface of the shell of *A. ferussacianus* which could possibly offer the binding sites for cations under investigation.

KEYWORDS: heavy metals, biosorption, shell, wastewater treatment, kinetics, FTIR.**INTRODUCTION**

The contamination of toxic heavy metals, such as nickel lead (Pb II), (Ni II), cadmium (Cd), etc. has emerged as a serious ecological threat in the world today. These hazardous metal ions tend to travel through food chain and potentially can damage the health of any organisms at any trophic level (Paknikar *et al.*, 2003). There may be various sources by which heavy metals poured to the water bodies, such as anthropogenic as well as natural. Human activities in recent decades have contributed significantly to this problem (Francis, 1994). It is mainly on account of rapid urbanization and industrialization especially in last few decenniums along with aquatic ecosystem has polluted the environment (Azarbad *et al.*, 2010; Yuzeroglu *et al.*, 2010). The entire scenario particularly in developing countries is alarming (Boran and Altinok, 2010; Shariati *et al.*, 2011).

Heavy metal pollutants are being dumped into aquatic bodies by a number of industrial sources, such as electroplating, chemical manufacturing, fertilizer industries, tannery operation, metallurgical industries, mine drainage, etc. (Shahzad *et al.*, 2015). There are a

number of industrial activities responsible for the addition of Pb (II) in the environment, such as burning of fossil fuels, smelting of sulphide ores, battery manufacturing and metal plating industries (Abollino *et al.*, 2003). Automobiles are also a cause of Pb (II) in environment. Recently, the usage of Pb (II) has increased tremendously. It is estimated that it was used from 4.5 million tons to 6.5 million tons during period 1970 to 2000 in world (Du *et al.*, 2011).

Recently, biosorption has emerged as an effective tool in this prospect. Biosorption seems to have many advantages over other traditionally used technologies, such as like less expenditure, higher efficiency for metal removal and so much so it is environment friendly (Volesky and Holan, 1995). Biosorption is a physical process in which dead biomass (biosorbent) is used. Solution is allowed to pass over biosorbent and the heavy metal cations are allowed to passively adsorb to its surface (Rangsayatorn *et al.*, 2002). The biosorption process involves a solid phase (sorbent or biosorbent; usually a biological material) and a liquid phase (solvent,

normally water) containing a dissolved species to be sorbed (Sorbate, a metal ion).

The present studies deal with the use of shell of a freshwater mussel, Cylindrical Paper shell mussel (*Anodontoidea ferussacianus*) in biosorption of heavy metals, such as Pb (II). It is cosmopolitan in distribution and lives in small creeks and the headwaters of larger streams in mud and sand (Burch, 1975).

The main objective of this study is to explore the potential of fresh water mussel shell powder to remove metal ions such as Pb (II). This metal ion has been selected in view of their high prevalence in aquatic bodies as is evident from a number of previously performed studies (Du *et al.*, 2011). The effect of various physico-chemical parameters, such as pH, temperature, metal concentration and sorbent dosage, etc. will also be studied. The data will also be elucidated to various adsorption models, kinetic models, etc.

MATERIALS AND METHODS

3.1. Materials

3.1.1. Site Description and Sampling

The freshwater bodies around Bambanwala Ravi Bedian (BRB) canal near town Daska, district Sialkot, Pakistan were surveyed and selected as sampling site. Thirty Freshwater mussels were collected and transported to General Research Laboratory, Department of Zoology, Govt. College University Lahore, Pakistan for further analysis and research.

3.1.2. Identification of Freshwater Mussels

Identification at species level was done by careful phenotypic analysis by using standard identification key (Freshwater Biology by Ward and Whipple) and was identified as *Anodontoidea ferussacianus* belonging to phylum Mollusca, class Bivalvia, order Unionoida, family Unionidae, genus *Anodontoidea* and species *Anodontoidea ferussacianus*.

3.1.3. Processing of Shell Biomass

Freshwater mussels were taken into stainless steel dish and were rinsed in tap water for 15 minutes to remove formalin. Dissection of freshwater mussels was done in order to isolate shells from soft body tissues. These samples were cleaned by brushing in water to remove any adhered materials. Shells were further treated with 0.02 M HNO₃ in order to remove any possible cations attached on the surface of shells. The samples were dried at 60°C up to a constant weight and then crushed by using ball mill. Crushed shell powder was passed through 300nm nylon mesh to obtain uniform sized biomass.

3.1.4. Preparation of Heavy Metal Solution

A stock solution of 1000 mg/L of Pb (II) was prepared and diluted to a solution of 500 mg/L concentration for further use. Erlenmeyer glass flasks (250 ml) were

washed with HNO₃ and after air drying were autoclaved for the experiment.

3.2. Methodology

3.2.1 Biosorption Studies

100 mL of Pb (II) was taken in 250 mL Erlenmeyer flasks. Two sets of three flasks were maintained for each metal solution, containing 0.5g, 1.0g and 1.5g of shell biomass. Thereafter, all the flasks were set for 3 hours on rotary shaker at 200 rpm. Samples of 5 ml were periodically collected after every 30 minutes. A constant pH for batch equilibrium sorption experiments was maintained by adjusting pH of the solution periodically with 0.1N NaOH and 0.1N HNO₃. The experiments were repeated at varying pH, such as 2, 4 and 6. Experiments were also performed at varying temperature of 20, 30 and 40°C. All the experiments were performed in triplicates.

3.2.2. Analysis of the Samples

Samples analysis for estimation of metal ion concentration was performed at the Department of Chemistry, Government College University, Lahore, by using Atomic Absorption Spectrometer, model, FAAS, Shimadzu AA-7000F.

3.2.3. Fourier Infra-red Transform Spectroscopy (FTIR)

For the evaluation of binding sites, FTIR was performed in which following samples were subjected.

- Shell biomass cleaned by HNO₃ treatment and deionized water (control).
- Lead loaded (Pb (II) - loaded) shell biomass.

All spectra obtained after FTIR were normalized and baseline corrected with Perkin-Elmer IR Data management software. Data were then exported to Microsoft Excel 2007 and all spectra were area normalized. The FTIR spectroscopy is an important analytical technique which detects the vibration characteristics of chemical functional groups present on adsorbent surfaces.

These analytical studies were performed at the Department of Chemistry, GC University Lahore, Pakistan by using FTIR, model MIDAC M 2000.

BIOSORPTION OF LEAD Pb (II) BY *Anodontoidea ferussacianus*

The efficiency of the biosorption is greatly affected by the physico-chemical properties of the solutions, such as temperature, pH, initial concentration, etc. (Volesky, 2003). The biosorptive capacity of *A. ferussacianus* was studied under variable conditions.

4.1.1. Effect of pH

The biosorption of Pb (II) was studied at varying pH, such as 2, 4 and 6. The maximum uptake of Pb (II) was found to be 130 (26%), 155 (31%) and 180 mg/L (36%) at pH of 2, 4 and 6 respectively (Fig. 4.1). Here pH 6 was found to be optimum.

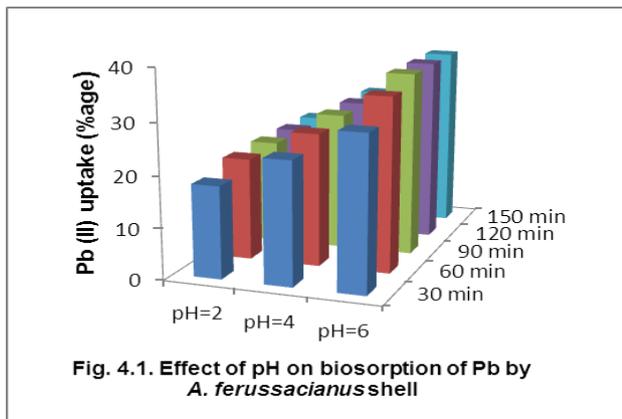


Fig. 4.1. Effect of pH on biosorption of Pb by *A. ferussacianus* shell

4.1.2. Effect of Temperature

The maximum uptake of Pb (II) was found to be 115 (19%), 200 (36%) and 180 mg/L (32%) at temperatures of 20, 30 and 40°C respectively (Fig. 4.2). In all these experiments, equilibrium was found to achieve in 90 min. Here optimum temperature was found 30°C.

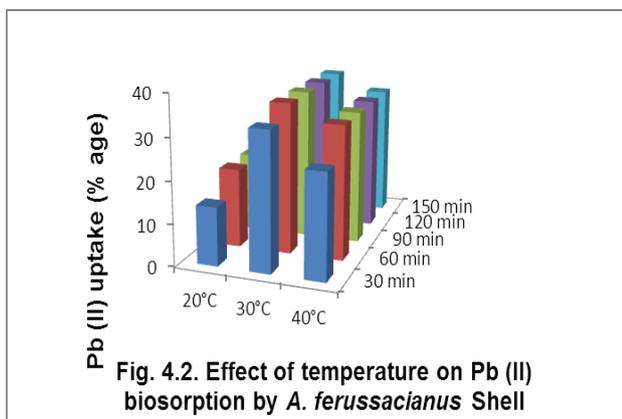


Fig. 4.2. Effect of temperature on Pb (II) biosorption by *A. ferussacianus* Shell

4.1.3. Effect of Contact Time and Biomass Quantity

Under biomass concentration of 5 mg/L, the maximum uptake of Pb (II) ions after 30 min was found to be 50 mg/g (10%) and after 60 min, it achieved equilibrium

with 75 mg/g (15%) and beyond this point no further uptake was noticed and under biomass concentration of 10 mg/L, the maximum uptake of Pb (II) ions after 30 min was found to be 105 mg/g (21%) and after 60 min, it achieved equilibrium with 125 mg/g (25%) and beyond this point no further uptake was noticed.

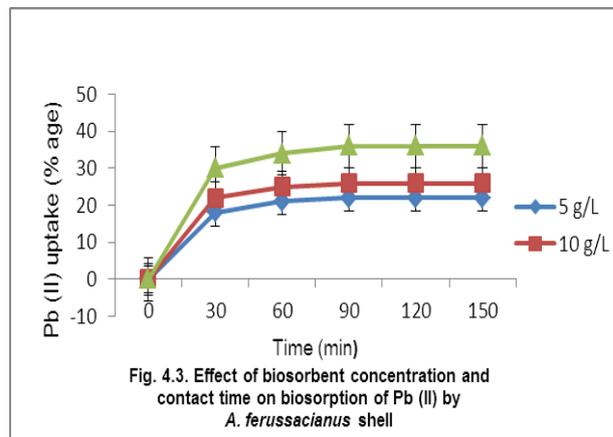


Fig. 4.3. Effect of biosorbent concentration and contact time on biosorption of Pb (II) by *A. ferussacianus* shell

On other hand when biomass concentration of 15 mg/L, the maximum uptake of Pb (II) ions after 30 min was found to be 140 mg/g (28%) and after 60 min, it achieved equilibrium with 155 mg/g (31%) and beyond this point no further uptake was noticed (Fig. 4.3).

4.1.4. Langmuir Isotherm

Plots of inverse of the equilibrium concentration of Pb (II) ions biosorption by the sorbent (1/qe), versus inverse of equilibrium concentrations of the Pb (II) in the aqueous solution (1/Ce) at the various ion concentrations in the solution were drawn (Fig. 4.4). Maximum adsorption capacity (q_{max}) of Pb (II) biosorption by *A. ferussacianus* was found to be 11.7 mg/g, b as 5 L/mg and R² as 0.94 (Table. 4.1).

Table 4.1: Langmuir Isotherms’ constants for the sorption of Pb (II) and Ni (II) ions by the investigated by *A. ferussacianus* shell biosorbent.

Biosorbent	Pb (II)							
	q _{max} (mg/g)	B (L/mg)	R ²	k	q _{max} (mg/g)	b (L/mg)	R ²	K
<i>A.ferussacianus</i> Shell	11.7	5	0.94	4.60	13.6	2.5	0.97	0.43

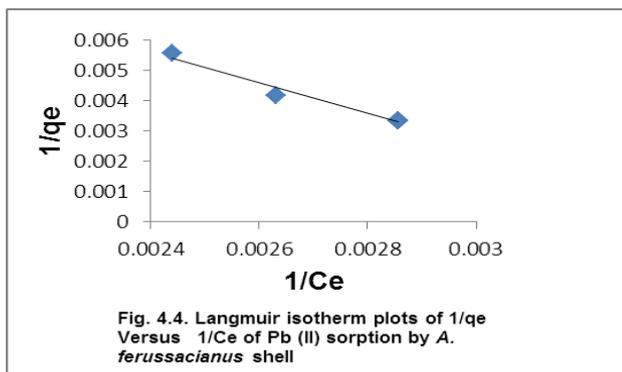


Fig. 4.4. Langmuir isotherm plots of 1/qe Versus 1/Ce of Pb (II) sorption by *A. ferussacianus* shell

4.1.5. Freundlich Isotherm

This isotherm was used to determine the adsorption intensity of the sorbent toward the heavy metal ions. A linear plot of ln qe versus ln Ce was drawn and values of intercept and slope were determined to determine Freundlich’s constants (Fig. 4.5). The value of N for Pb (II) biosorption by *A. ferussacianus* was found to be 0.01, K_F (saturation constant) was 1.51 and R² (regression coefficient) was 0.98 (Table. 4.2).

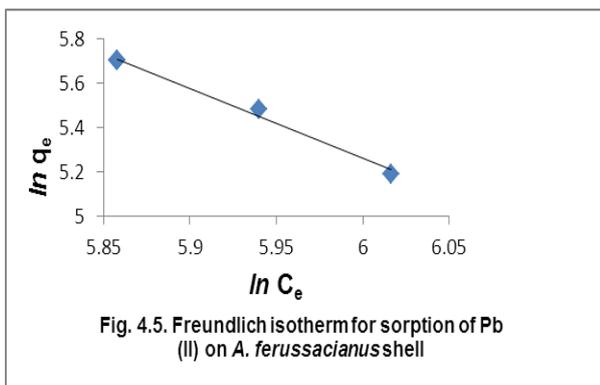


Fig. 4.5. Freundlich isotherm for sorption of Pb (II) on *A. ferussacianus* shell

Table 4.2: Freundlich Isotherms' constants for the sorption of Pb (II).

Biosorbent	Pb (II)		
	n	K _F	R ²
<i>A.ferussacianus</i> Shell	0.01	1.51	0.98

4.1.6. Temkin Isotherm

Linear plot of q_e versus $\ln C_e$ was drawn and the values of intercept and slope were calculated (Fig. 4.6). Values of Temkin's constants determined thereafter. Value of K_T (equilibrium binding constant) for Pb (II) by *Anodontoides ferussacianus* was found to be 6.06, B (Temkin's constant) was 0.92 and R^2 (regression coefficient) was found 0.96 for Pb (II) (Table. 4.3).

Table 4.3: Temkin Isotherms' constants for the sorption of Pb (II).

Biosorbent	Pb (II)		
	K _T	B	R ²
<i>A. ferussacianus</i> Shell	6.06	0.92	0.96

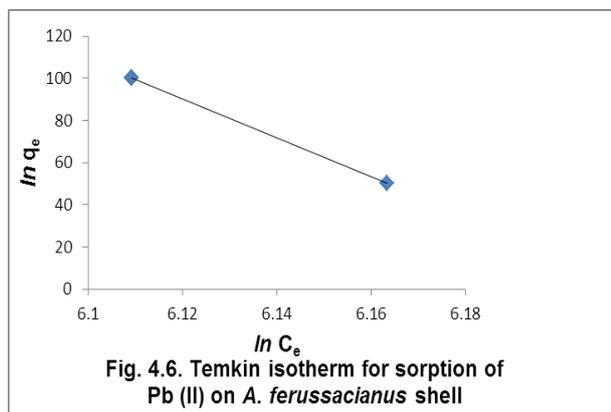


Fig. 4.6. Temkin isotherm for sorption of Pb (II) on *A. ferussacianus* shell

4.1.7. Pseudo-Second Order Kinetic Model

Pseudo-second order model was employed for the biosorption of Pb (II) by *A. ferussacianus* and was found to be well fitted for the data obtained from the experiment. A linear plot of t/q_{eq} versus t was drawn and intercept and slope of the data was calculated to determine the constants of pseudo-second order kinetic model (Fig. 4.7). Value of q_{eq} was found to be 2.22, K_2 was 0.13 and R_2 as 0.96 (Table. 4.4).

Table 4.4: Pseudo-second order kinetic constants for the biosorption of Pb (II).

Biosorbent	Pb (II)		
	q _{eq} (mg/g)	K ₂	R ²
<i>ferussacianus</i> Shell	2.22	0.13	0.96

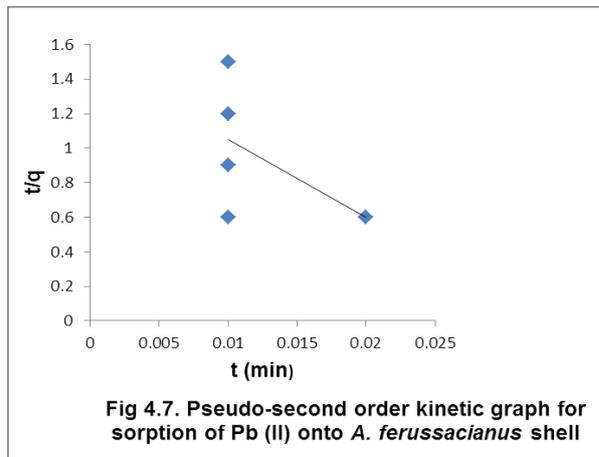


Fig 4.7. Pseudo-second order kinetic graph for sorption of Pb (II) onto *A. ferussacianus* shell

4.1.8. FTIR Spectroscopy

In order to investigate binding sites of Pb (II) on the surface of biosorbent was carried out by Fourier Transform Infra-Red (FTIR) Spectroscopy. FTIR spectrum showed the shift in peaks of 1123 (unloaded samples) to 1154 (Pb loaded samples), 1424 (unloaded samples) to 1471 (Pb loaded samples), 1642 (unloaded samples) to 1785 (Pb loaded samples), 2946 (unloaded samples) to 2932 (Pb loaded samples), 3470 (unloaded samples) to 3548 (Pb loaded samples) and 3348 (unloaded samples) to 3694 (Pb loaded samples). These shifts are characteristic of electronegative functional groups, such as cyanide (-C-N), carbonyl (C=O), amine (-N-H), carboxylic (COO⁻) and alkyl (-C-H₂) respectively (Table. 4.5).

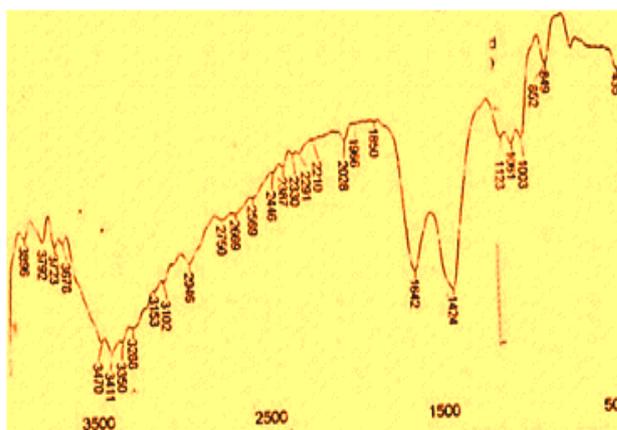


Fig. 4.15: Untreated FTIR spectra of *A. ferussacianus* shell (Control).

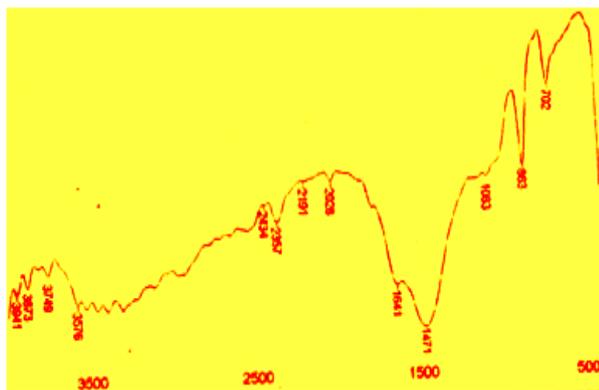


Fig. 4.17: Pb (II) treated FTIR spectra of *A. ferussacianus* shell.

Table 4.5: Shifts in wavelengths (Cm^{-1}) of FTIR absorption for Pb (II) and Ni (II) ions biosorption by the *A. ferussacianus* shell.

Pb (II) Treatment		
Unloaded	Loaded	Functional group
1123	1154	-C-N<
1424	1471	Symmetrical bending of CH_3 of acetyl moiety
1642	1785	C=O Chelate stretching
2946	2932	Phenolic/ Carboxylic
3470	3548	-C=H
3448	3694	CH/NH

DISCUSSION

The potential of biosorption of Pb (II) by using biomass obtained from *A. ferussacianus* has been investigated. Fourier Transform Infra-red Spectroscopy (FTIR) was carried out to determine the binding sites for biosorption of Pb (II) ions. The outcomes of present studies will also be of immense interest for heavy metal pollution treatment and for removal of toxic metal, such as Pb (II) ions.

Biosorption Capacity of the Biosorbent

In present study, the influence of some important physico-chemical parameters, such as pH, contact time, temperature and biosorbent concentration etc. on biosorptive potential of Pb (II) ions by *A. ferussacianus* shell has been investigated. All these physico-chemical parameters have been found to affect the efficiency of biosorption.

Effect of pH

It has been investigated that pH of solution has greatly affected the dissociation of surface of *A. ferussacianus* shell biomass and chemical properties of solution of heavy metals. For example, pH influenced hydrolysis, oxidation-reduction reaction, and complex formation by ligand and precipitation. Many earlier studies on biosorption of heavy metals by using dead biomass obtained from different organisms have confirmed this evidence (Arief, *et al.*, 2008; Guo, *et al.*, 2008). Sheng *et al.*, (2004) reported that pH affected the metal uptake

because it is concerned with functional groups on the surface of biomass and chemical parameters of the solution. Equilibrium of system is also influenced by pH (Romera *et al.*, 2006).

The influence of pH of solution on biosorptive capacity is given by below equation (Arief *et al.*, 2008).

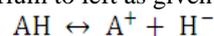
$$\text{pH} = \text{Ka} - \log \frac{[\text{AH}]}{[\text{A}^-]}$$

Where,

[AH]= Concentration of protonated surface functional groups.

[A]= Concentration of deprotonated surface functional groups.

When the value of pH is smaller than pKa, there is shifting of equilibrium to left as given below,



$$K_a = \frac{[\text{A}^-][\text{H}^+]}{[\text{AH}]}$$

When protons are used then pH raised until it reaches the pka. The reverse trend is seen when pH is greater than the pka (Romera *et al.*, 2006).

In present study, the maximum uptake of Pb (II) ions was at optimum pH 6.0 (Fig. 4.1). The efficiency of sorption of Pb (II) increased with the increase in pH value because at higher pH, more ligands were available for Pb (II) ions binding whereas at lower pH, there was competition for active binding sites between protons and metal ions. At low pH, the amount of H^+ ions was high so Pb (II) ions had to compete with H^+ to get attached with surface functional groups of shell biomass. On the other hand, at high pH, due to decreased no. of H^+ in the solution, Pb (II) ions may have enhanced probability to bind with free binding sites. However, in alkaline pH, Pb (II) may tend to precipitate in solution, thus decreasing the quantity of soluble sorbent available for sorption.

A number of previously performed similar studies have been performed. Optimum pH for sorption of Pb (II) by oyster shell was reported as 6 (Du *et al.*, 2011). Similarly, optimum pH for biosorption of Cu (II) by bivalve mollusks was reported as 5 (Liu *et al.*, 2009). This is in agreement with the present study in which optimum pH for Pb (II) was 6. whereas, optimum pH for uptake of Pb (II), Ni (II) and Cd (II) ions was reported between achieved 4.0-6.0 by using biosorbent, African giant land snail, *Archachatina marginata* (Jideowno *et al.*, 2007).

Effect of contact time

In present study, optimum contact time for Pb (II) ions have been found as 90 min. Up to first 30 minutes, initially uptake of Pb (II) ions was rapid, followed by slower uptake and finally achieving equilibrium concentrations after 90 minutes (Fig. 4.3) with no further rise in uptake. This implies that initially, a number of free binding sites were available for Pb (II) ions which were occupied later on, and the number of unoccupied

sites decreased with the passage of time. These findings are in agreement with the previously reported optimum contact time of 90 min in case of Cu (II) removal by bivalve mollusk (Liu *et al.*, 2009).

Effect of temperature

Temperature affected the sorption of Pb (II) ions. The optimum temperature was 30°C for uptake the metal ions under study (Fig. 4.2). The uptake values of Pb (II) ions were observed lower at 20°C. This decreased sorption efficiency of biosorbent might be due to the shrinkage of surface at lower temperature. At 30°C, sorption was improved. However, at 40°C biosorption values again decreased. It is believed that sorption reactions are normally exothermic therefore; higher temperature could damage the active sites of the biomass (Ozer and Ozer, 2003). Previously a number of studies regarding the effect of temperature on metal uptake have been carried out. Jideowno *et al.*, (2007) reported that the optimum temperature of the removal of Pb (II), Ni (II) and Cd (II) ions ranged from 30-45°C by using shell of African giant land snail (*Archachatina marginata*). Liu *et al.*, (2009) studied the maximum of uptake of Cu (II) at optimum temperature of 25°C by using bivalve mollusk shell biosorbents. The plausible explanation of disagreement of these studies with the present study might be variation in shell biochemistry in different mollusk species.

Effect of biosorbent concentration

In the present study, optimum biomass concentration for metal ion uptake was found at 15 g/L whereas for q_e values, optimum biomass was 5 g/L in case of Pb (II) ions (Fig.4.3). The biosorptive potential of sorbent was directly proportional to the concentration of biomass (Aydin *et al.*, 2008). However, on the other hand, small sized biosorbent provide large surface area which is available for sorption and are easier to dissolve compared with the large particles. This implies that the q_e value of biosorption (uptake value per biomass unit) tends to decrease with the increase in biomass. The greater amount of sorbent in solution has provided a large number of active sorption sites, resultantly increasing the number of available functional groups (Tunali *et al.*, 2006).

Biosorption equilibrium isotherms

There are a number of traditionally employed sorption isotherms, such as Langmuir, Freundlich and Temkin isotherms used to evaluate the biosorption of metal ions. In the present study, experimental data have been found to obey Freundlich isotherm more than any of the above mentioned models (Fig. 4.4, 4.5, 4.6) for both the metal ions brought under investigation (Table 4.1, 4.2 and 4.3). This implies that the biosorbent used in this study, *A. ferussacianus* shell shows multilayer sorption rather than monolayer sorption. These findings are in agreement to the previously reported similar studies in which shells of oysters and clams were used as biosorbent (Du *et al.*, 2010).

Biosorption kinetics

The experimental data derived in the present study has also been subjected to pseudo-second order kinetic models, used to determine rate limiting step. It has been found that the biosorption dynamics can be explained by different steps, such as movement of solute from bulk solution to the external surface of biosorbent and biosorption of solute on the interior surfaces of the biosorbent. Kinetic studies of Pb (II) ions on shell biosorbent showed a fast initial sorption phase which was followed by slow and partial equilibrium process (Prito *et al.*, 2003).

This fast initial sorption phase might be due to fact that in beginning, a large number of free binding sites were available whereas these sites were increasingly becoming occupied with the increase in contact time. Data obtained from present studies was well fitted to a pseudo second order kinetic model (Table 4.4). This mechanistic explanation of this rate determining reaction can be given in the following expression,

M^{+2} ions \rightarrow biomass

Where,

M^{+2} = metal ions (cations) being accumulated on shell biosorbent.

The values of regression coefficient in cases of both the metal ions studied, Pb (II) indicate the suitability of this data to fit on the pseudo-second order kinetic model (Table 4.4).

Binding Sites for Biosorption of Metal Ions

Fourier Transform Infra-red spectroscopic (FTIR) spectra have been found to confirm the presence of electronegative functional groups onto the surface *A. ferussacianus* shell those offer binding sites for metal ions, such as Pb (II) ions.

FTIR spectroscopy was used to evaluate and characterize functional groups on sorbent surface. Table 4.5 lists the functional groups present in biomass under investigation. The shifting of peaks of spectra in the samples loaded with Pb (II) from those unloaded (Fig. 4.15) has confirmed the presence of various functional groups. These groups are numerous and are electronegative, such as cyanide, carbonyl, amine, carboxylic and alkyl, etc. These groups carrying negative charge can directly bind to metal ions. These findings are in agreement with previously performed studies (Yaqub *et al.*, 2012).

The presence of similar functional groups, such as -OH, NH, C=O and S=O were also reported on the surface of other bivalve mollusks (Liu *et al.*, 2009). The investigation of various functional groups on shell surface greatly helped to understand the surface binding mechanism of Pb (II) ions.

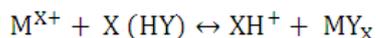
The biochemical composition of *A. ferussacianus* may well be appreciated for holding the above mentioned functional groups. In mussels and potentially most

mollusks, the surface layer in the shell has an organic framework of the proteins, proteoglycans, and polysaccharides, such as chitin; the underlying (prismatic) layer uses MSI31 proteins to construct its framework. This too forms beta-pleated sheets (Sudo *et al.*, 1997). Since acidic amino acids, such as aspartic acid and glutamic acid, are important mediators of biomineralization, shell proteins tend to be rich in these amino acids (Tong *et al.*, 2004). Aspartic acid, which can contribute up to 50% of shell framework proteins, is most abundant in calcitic layers, and also heavily present in aragonitic layers. Proteins with high proportions of glutamic acid are usually associated with amorphous calcium carbonate (Ahalya *et al.*, 2003). It is highly critical to note that both the above mentioned amino acid, aspartic acid and glutamic acid are rich in electronegative functional groups, such $-\text{COO}^-$, $-\text{OH}$, $-\text{NH}$, etc. which may offer cation binding, such as Ni^{++} and Pb^{++} , etc.

5.3. Mechanism of Biosorption

Many processes have been suggested to explain the biosorption, such as surface adsorption, chelation, complexation, surface precipitation, reduction and transfer anion from aqueous to solid phase (Sposito, 1984).

Ion exchange is a reversible process in which ions are exchanged between a solution and solid. This technique is also widely used in industrial processing (Han *et al.*, 2006). The mechanism of ion exchange can be generally expressed,



Where,

HY= total number of sites on surface of solid

M^{X^+} = metal ion

MY_X = sorbet metal ion

The ion exchange equilibrium constant can be represented by following equation (Arief *et al.*, 2008).

$$K_{\text{IE}}^{\text{H}} = \frac{[\text{H}^+][\text{MY}_\text{X}]}{[\text{M}^{\text{X}^+}][\text{HY}^{\text{X}}]}$$

Ofomaja *et al.*, (2007) proposed the process of ion exchange as main biosorption mechanism.

Chelation is another important mechanism of metal binding. It is defined as the chemical process of forming a ring by forming one or more hydrogen bonds. Among all the functional groups reported on the surface of the shell, amino group is most operational or efficient for removal of heavy metals because it chelates metal cations by forming hydrogen bonds (Deng *et al.*, 2007).

CONCLUSION AND RECOMMENDATIONS

The present study has clearly declared the shell of *A. ferussacianus* can be sued as potential biosorbent for the removal of heavy metals, such as Pb (II) etc. The idea of the exploitation of mollusk shell is relatively newer to present day researchers and the shell biomass of *A. ferussacianus* has been used for first time. The growing

understanding in this regard may open new horizons of zooremediation. Visceral mass of many of these mollusks is already widely used in food industry; speculations can be established that their shell may also be brought to usage in wastewater treatment technology as biosorbents. There are thousands of species of gastropods, bivalves and other mollusks, soft body parts of some of which are edible and still many unexplored. The shell of all such animals can be tested for their biosorptive capacities and it is most likely that biochemistry of many of these may favor them to prove as promising candidates in the race of biosorbents. Frontiers are yet to be explored to exploit the biochemistry of thousands of mollusk shells that have not by far been tested.

On the basis of the findings of the present study, it is recommended that more species can be tested for their biosorptive capacity of heavy metal ions. The usage of these biosorbent will be cost-effective as well as eco-friendly. It is also recommended that novel biosorbent with better efficiency may be developed either by the combination of biomass from different species or by hybridization of shell biomass with already established synthetic biosorbents. In future considerations may be undertaken to explore the biochemical ingredients' detailed profile of mollusk shell, such as that of mussels and oysters, etc. and biosorbents may be developed even with improved efficiency.

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