Optimization of Conditions for Biosorption of Chromium and Cadmium by Shell of *Anodontoides ferussacianus*

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Authors' contributions

This work was carried out in collaboration between all authors. Author SS designed the study, performed the statistical analysis, wrote the protocol and wrote the first draft of the manuscript. Authors AY and MNA managed the analyses of the study. Authors MH, UA and NS managed the literature searches. All authors read and approved the final manuscript.

Original Research Article

ABSTRACT

The biosorption of chromium [Cr (VI)] and cadmium [Cd (II)] ions using dead biomass of bivalve mollusk shell, *Anodontoides ferussacianus* was studied. Effect of various physico-chemical parameters was determined. Optimum pH was 4, temperature was 30°C, biosorbent concentration was 15 g/L and sorbate-sorbent contact time was 90 min with equilibrium concentration (qeq) of 300 mg/g and 280 mg/g for Cr (VI) and Cd (II) respectively. Many models of adsorption isotherm were used like Temkin, Langmuir and Freundlich. Regression coeffient (R2) values of Cr (VI) and Cd (II) were 0.99 & 0.97 for Langmuir, 1 & 0.99 for Freundlich, 0.99 & 0.97 for Temkin respectively. Vaious parameters of these models were also determined for Cr (VI) and Cd (II) with Langmuir's qmax= 12.6 and 14.4 mg/g respectively and Fruendlich's KF= 1.6 and 1.18 respectively. This shows multilayer sorption by *A. ferussacianus* shell for Cr (VI) and Cd (II). Kinetic model of Pseudo-

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second order revealed the process of Kinetics [K2= 0.19 & 2.4 and R2=0.96 & 0.93 for Cr (VI) and Cd (II) respectively]. Additionally, shifts in FTIR (Fourier Transform Infra-red Spectroscopy) spectra indicated the binding sites of specific functional groups (–OH, -NH, C=O and S=O) for Cr (VI) and Cd (II) on biosorbent surface.

1. INTRODUCTION

Industrial revolution has accelerated addition of pollutants into the environment in recent decades. These contaminants tend to enter not only in aquatic fauna and flora but also they travel through food chain to affect terrestrial life forms. Another way they can affect human population is through groundwater contamination that is consumed by drinking [1].

Leading supplies of heavy metals consist of wastes from metal finishing industries and electroplating, chemical manufacturing, battery manufacturing, fertilizer industries, pigment manufacturing industries, tannery operations metallurgical industries, mine drainage, leakages from contaminated ground water and landfills [2]. Heavy metal pollutants, such as chromium [Cr (VI)] and cadmium [Cd (II)] have been entered in aquatic environment due to human activities, like for chromium [Cr (VI)] finishing industries and electroplating, chemical manufacturing, fertilizer industries, pigment manufacturing industries, tannery operations metallurgical industries, mine drainage, leakages from contaminated ground water and landfills for cadmium [Cd (II)] [3] Cadmium is utilized in plastic industries and in metal plating and batteries and manufacture pigments [4,5]. Recently, different strategies are being used to remove these heavy metals from aqueous solution such as, chemical precipitation, electrolytic recovery, ion exchange/chelation and solvent extraction/liquid membrane separation and bioaccumulation [6]. The biosorption is one the most reliable method, such as cost-effective and reliable technology.

Biosorption is a physiochemical process in which heavy metals are removed by adsorption with the outer surface of biomass. There is difference between Biosorption and Bioaccumulation. Biosorption does not need energy because it is metabolically passive process. Structure or composition of outer surface of biomass and also kinetic equilibrium controls the attachment of Cr and Cd on the surface of biomass [7]. On the other hand bioaccumulation is the process to use energy for attachment of heavy metals as well as this process need living organism [8]. Bioaccumulation and Biosorption are happening naturally in all living organisms [9]. It has been proved by experiment that bio- sorption is happening 13-20% more in dead organism as compare to in living [10]. Biosorption is the process to attached heavy metals on the specific ionic site of biosorbent naturally, although bioaccumulation need energy for attachment of heavy metals ions which means its bioaccumulation is different from biosorption. Bioaccumulation is the process which required living organism while biosorption did not need living organism [11]. The underlying fact is that biochemistry of mollusk shell showed that it has chitin group, calcium carbonate, and also some functional group such as, -OH, C=O, S=O and –NH are high which can possibly provide site of attachment for the cation, such as Cd (II) and Cr (VI) [12]. Exploitation of mollusk shell in wastewater treatment technology may hence be cost-effective.

2. MATERIALS AND METHODS

The freshwater mussel (Anodontoides ferussacianus) cylindrical paper shell biomass was collected from Bambanwala Ravi Bedian (B.R.B) canal near Daska, district Sialkot, Pakistan. The shells were removed and washed thoroughly by using distilled water with brush to remove particles from the surface. These shells were treated with 0.02 M HNO3 to remove any possible cations on surface. Finally, these samples were washed with distilled water, dried in oven at 60°C up to a constant weight and ground up to a particle size of 300 nm by nylon mesh [13].

Solution of chromium [Cr (VI)] and cadmium Cd (II) was prepared by dissolving 3.86 g of potassium dichromate-6-hydrate [K2Cr2O7.6H2O] in distilled water up to a volume of 1000 mL. Thereafter, 500 ppm of the same

was prepared by serial dilution and for cadmium 1.79 g of cadmium chloride-1-hydrate (CdCl2.H20) in distilled water up to a volume of 1L. 500 ppm of the same was prepared by serial dilution Solution of 500 ppm. 100 mL of Cr (VI) and Cd (II) solutions were taken in 125 mL Erlenmeyer flasks [at concentrations of 100, 200 and 300 ppm of Cr (VI) and Cd (II)]. The solutions were set at the pH of 4.0 for Cr (VI) and Cd (II) by using 0.1 N HNO3 and 0.1 N NaOH and not controlled afterwards.

Biomass concentrations of 5, 10 and 15 mg/L were introduced in the above mentioned concentration of Cr (VI) and Cd (II) solutions each in 125 mL Erlenmeyer flask. Then all the flasks were set on rotatory shaker at 25°C and at 180 rpm (rotation per minute) for 3 hours. Samples (5 mL each) were periodically collected after every 30 minutes. After collecting samples, each sample was poured in BD syringe. Each sample was then passed through 0.25 nm Nylon Syringe Filters (Fisher Scientific, USA). The filtrate was then preserved for advanced analysis. All the experiments were performed in triplet. Analysis of metal ion concentrations were done at the Department of Chemistry, GCUL, by using Atomic Absorption Spectrometer, model, FAAS, AA-7000F.
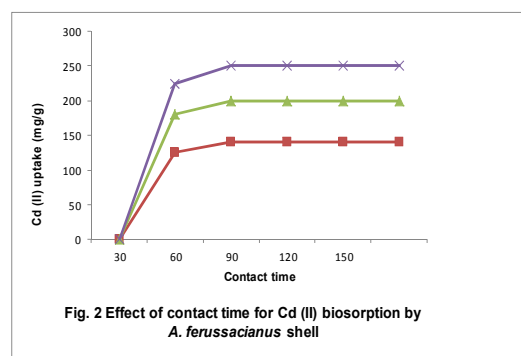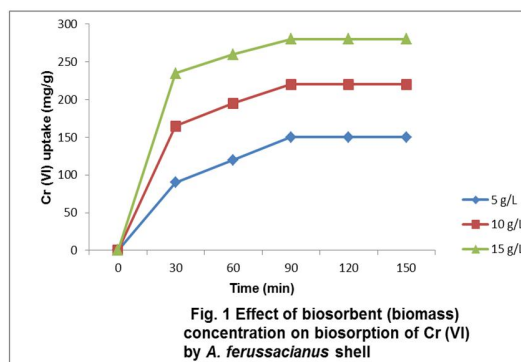
Fourier Transform Infra-Red Spectroscopy (FTIR) was performed to study freshwater mussels shell samples of untreated (control) as well as treated samples. Cr (VI) treated and Cd (II) treated samples were brought under study. Burker instrument (Model NO, ALPHA-P) was used to obtain spectra.

3. RESULTS AND DISCUSSION

Contact time play very important role for the absorption of Cr (VI) and Cd (II) in aqueous solution. Maximum absorption has been observed to 90 minutes while 30 minutes revealed lowest adsorption. Absorption of metals ions up to 180 minutes was not seen. Absorption capacity of Cr (VI) and Cd (II) by *A. ferussacianus* at different contact times, viz: 30, 60, 90, 120, 150 and 180 minutes showed in Figs. 1 and 2. Maximum time required for absorption is 90 minutes.

To get qmax maximum absorption time is 90 minutes. It is evident from the results that optimum time to attain qeq was 90 min for both, Cd (II) and Cr (VI) ions biosorption by A. ferussacianus shell. Whereas, initially (during the

first 30 min.), rapid cation uptake, slowing down importantly after the first 60 min. The similar results were reported by the previous studies [14]. The plausible explanation of this is that at the start of reaction, large number of binding sites on shell surface was available for cation binding. This resulted in the transfer of many solute molecules from solid to bulk phase. Also, the increase time diminishing removal of metal ions increase because intra- particle diffusion process dominating over adsorption [15,16] After 90 min, the binding sites were fully saturated with the solute binding.

Fig. 1 Effect of biosorbent (biomass) concentration on biosorption of Cr (VI) by *A. ferussacianus* shell

Fig. 2 Effect of contact time for Cd (II) biosorption by *A. ferussacianus* shell

Another factor for biosorption is biomass concentration. More biomass concentration more biosorption of heavy metals observed. The biosorption capacity of sorbents was found to increase with increase of biomass concentration. However, the amount adsorbed per unit mass decreased. In the present study, A. ferussacianus shell biosorbent, showed maximum uptake at 15 mg/L, followed by 10 and 5 mg/L. On the other hand, adequate qeq at 5 g/L concentration as compared to 10 g/L and 15 g/L, per unit mass were calculated. This could be explained as an effect of a partial collection of biomass at higher biomass concentration, which result in a decrease in effective surface area for the biosorption [17].

Specific metal uptake can also be affected by amount of biomass in solution, because more functional groups or adsorption sites are available in case of more adsorbent. Similar findings had been reported by other studies as well [18,19]. However, three concentrations of biomass like 15 mg/L, 10 mg/L and 5 mg/L used in the present investigation, 15 mg/L showed maximum biosorption. It concludes adsorption of cations per unit mass is maximum [20].

3.1 Influence of pH

The pH of the solution seems to have an important effect on dissociation of cations onto the surface of *A. ferussacianus* shell, such as complexation hydrolysis, by organic and/or inorganic ligands, redox reactions, and precipitation, as well as the speciation and biosorption availability for heavy metals. Relatively fewer studies have been performed in which m ollusk shells have been employed as biosorbent of toxic metal ions. However, previously performed similar studies reported varying results. In case of lead biosorption, the uptake increased from 2.3mg/g at pH 1 to 18.33 mg/g at pH 4 and when pH was increased further, uptake was found to decline by 5 mg/g at pH 6 [21].

Fig. 3 Effect of pH on biosorption of Cd (II) by
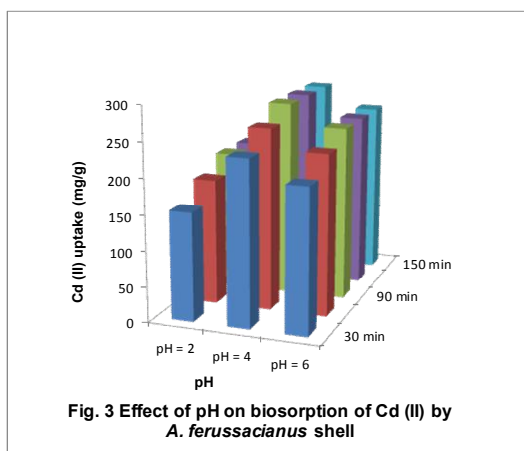***A. ferussacianus* shell**

Fig. 3 shows optimum pH for Cd (II) removal has been recorded as 4. This is in agreement with previously performed studies for biosorption with different bio-sorbents, such as on snail shell, crab shell etc. [22] With the decrease of pH up to 2, the uptake was reduced up to 30%. On the other hand, increase of pH also was reduced to 50%. These findings are in agreement with earlier reported biosorptive values of Cu (II) by

oyster shell [23] Optimum pH for Ni (II) sorption by crab shell was reported as 6 [8].

Fig. 4 Effect of pH on biosorption of Cr (VI) by
***A. ferussacianus* shell**
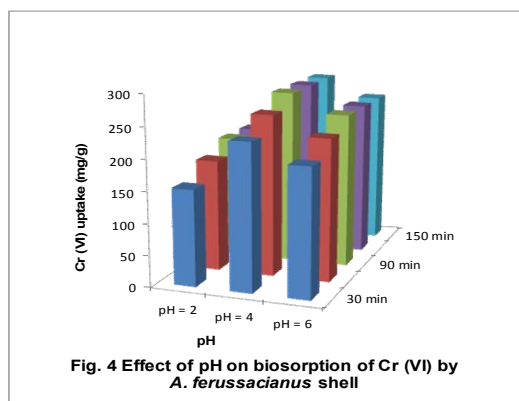
The plausible reason for this may be the difference of the biosorbent and sorbate used. Variation in the specific functional groups are residing on the sorbent surfaces are responsible for such behavior. Several other researchers have determined similar trends as regards pH effect on biosorption by shelled animals. Investigation of Pb (II), Cd (II), and Ni (II) sorption by chitosan (prepared from giant snail shell, *Archachatina marginate)* was conducted in the pH range of 2.0 – 6.0. Increase in the pH from 2 to 6, resulted in the increase of Cd (II) uptake.

Fig. 5 shows maximum absorption capacity of Cr (VI) ions by biosorbent was studied to be optimum at pH 4.0. At higher pH, exalted metal (at pH 4.0) sorption was applicable to the increase in the number of vacant ligands (binding sites) for metal ion binding, whereas the lower percentage of sorption of Cr (VI) ion onto sorbent at elevated pH (5.0, 6.0, and 7.0) might be ascribed to precipitation reaction which occurs pH 5.0-6.0.14.

3.2 FTIR Spectroscopy

Figs. 5 and 6 in order to investigate loaded and unloaded bio-sorbent with binding sites of Cr (VI) on the surface of bio-sorbent was carried out by Fourier Transform Infra-Red (FTIR) Spectroscopy. FTIR spectrum showed the shift in peaks of 1061 (unloaded samples) to 1083 (Cr loaded samples), 1424 (unloaded samples) to 1471 (Cr loaded samples), 3411 (unloaded samples) to 3576 (Cr loaded) samples), 3723 (unloaded samples) to 3749 (Cr loaded samples), 3896 (unloaded samples) to 3876 (Cr loaded samples). These shifts are characteristic

of electronegative functional groups, such as cyanide (−C- N), symmetrical banding of CH3 of acetyl moiety, carboxylic (COO-), OH stretch group, amine (-N-H), respectively.

Fig. 7 to investigate binding sites of Cd (II) on the surface of biosorbent was carried out by Fourier Transform Infra-Red (FTIR) Spectroscopy. FTIR spectrum showed the shift in peaks of 3470 (unloaded samples) to 3455 (Cd loaded

samples), 1642 (unloaded samples) to 1530 (Cd loaded samples), 1424 (unloaded samples) to 1408 (Cd loaded samples), 852 (unloaded samples) to 994 (Cd loaded samples), 1637 (unloaded samples) to 1631 (Cd loaded samples). These shifts are characteristic of electronegative functional groups, such as –OH, -NH, C=O chelate stretching, symmetrical banding of CH_3 of acetyl moiety, and C=O, -C-H respectively.
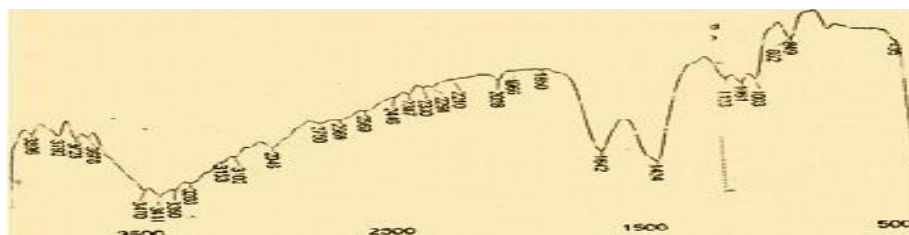

Fig. 5. Untreated FTIR spectra of *A. ferussacianus* shell (Control)

Fig. 6. Cr (VI) loaded FTIR spectra of *A. ferussacianus* shell

Fig. 7. Cd (II) loaded FTIR spectra of *A. ferussacianus* shell

FTIR absorption wavelength (Cm-1) for Cd (II) ion and Cr (VI) ions biosorption by the investigated freshwater Mussel shell biomass

	Cd (II)Treatment unloaded	Loaded	Functionlal group	Cr (VI)Treatment unloaded	Functional group (Loaded)	
A. ferussacianus	3470	**3455**	**-OH, -NH**	1061	**1083**	**-C-N**
	1642	**1530**	**C=O Chelate stretching**	1424	**1471**	**CH_3**
	1424	**1408**	**CH_3 acetyle moiety**	3411	**3576**	**COO⁻**
	852	**994**	**C=O**	3723	**3749**	**OH**
	1637	**1631**	**-C-H**	3876	**3876**	**NH**

3.3 Isotherms Modeling

Langmuir, Freundlich and Temkin's isotherms were applied to quantitatively illustrate the biosorption of metal ions by the test of mollusk.

3.4 Langmuir Isotherm

The Langmuir equation is given below:

qe = qeb.Ce/1+ (b + Ce)

The linearized form of this equation can be expressed as given below:

$$\frac{1}{q_e} = \frac{1}{q_{max}} + \frac{1}{b.q_{max}} \cdot \frac{1}{c_e}$$

Here,

Ce = Equilibrium conc. of heavy metal ion
qe = Equilibrium const. of metal ion on biosorbent surface (mg/g)
K2 = Saturation const. (mg/L)

Values of Ce, qe, and K2 were obtained by calculation of linear plot slope and intercept of 1/Ce versus 1/qe. The value of distribution coefficient (*k*) between aqueous solution and sorbent could be found out by following equation:

$$K = q_e / C_e$$

The reason of the Langmuir isotherm shows correlate the equilibrium data. Plots of inverse of the equilibrium concentration of Cr (VI) ions biosorption by the sorbent (1/qe), versus inverse of equilibrium concentrations of the Cr (VI) in the aqueous solution (1/Ce) at the various ion concentrations in the solution were drawn. Equal path is finish all round Cd (II) ions.

Figs. 8 and 9 exhibit maximum adsorption capacity (qmax) of Cr (VI) and Cd (II) biosorption by *A. ferussacianus* was found to be 12.06 and 14.04 mg/g respectively; "b" as 4.1 for Cr (VI) and 2.8 for Cd (II) and R2 as 0.99 for Cr (VI) and 0.98 for Cd (II). Value of distributional coefficient (k) was calculated as 5.70 and 4.98 for Cr (VI) and Cd (II) respectively.

3.5 Freundlich Isotherm

Freundlich isotherm was applied to evaluate multi-layered adsorbent. The equation given below is used for this theorem.
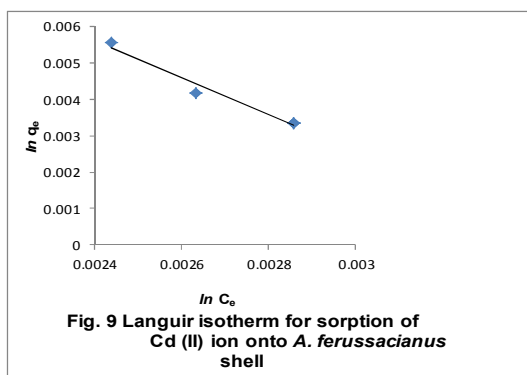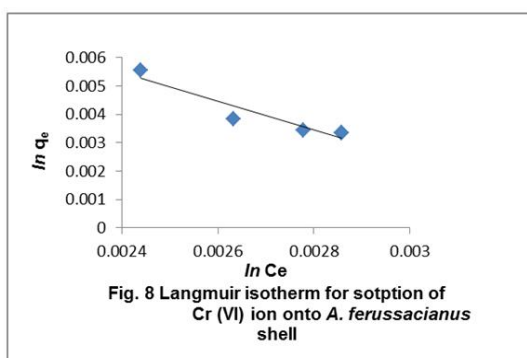
$$q_e = K_f C_e^{1/n}$$

This equation can be linearized as follows:

$$ln\ q_e = ln\ K_F + \frac{1}{n} ln\ C_e$$

Kf = Freundlich emperical const. / sorption capacity
1/n = emperical constant / sorption Intensity

This isotherm was used to determine the adsorption intensity of the sorbent toward the heavy metal ions. A linear plot of $ln q_e$ versus $ln C_e$ was drawn and values of intercept and slope were determined to determine Freundlich's constants.

Fig. 8 Langmuir isotherm for sotption of Cr (VI) ion onto *A. ferussacianus* shell

Fig. 9 Languir isotherm for sorption of Cd (II) ion onto *A. ferussacianus* shell

The value of n for Cr (VI) and Cd (II) biosorption by *A. ferussacianus* was found to be 0.04 and 0.06, KF (saturation constant) was 1.60 and 1.18 for Cr (VI) and Cd (II), and R2 (regression coefficient) was 1 and 0.99 for Cr (VI) and Cd (II) respectively. Figs. 10 and 11

3.6 Temkin Isotherm

Temkin isotherm was also employed as given by the following equation (Pahlevanzadeh et al. [24]):
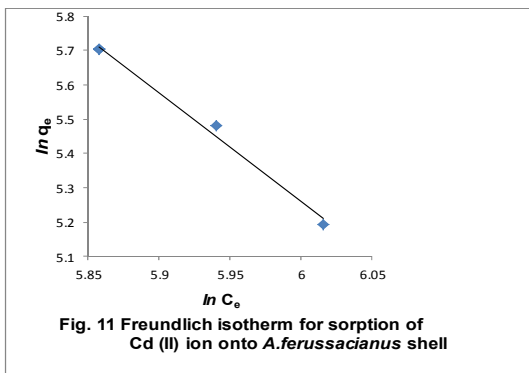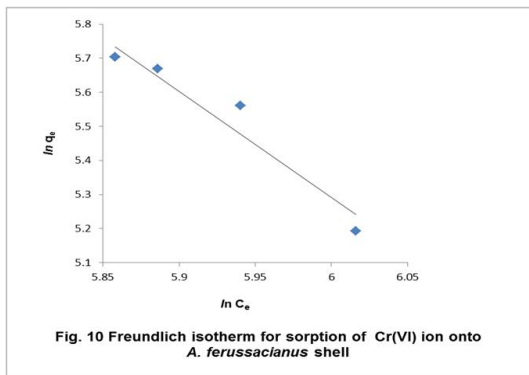
$$q_e = Bln(K_T C_e)$$

$K_T =$ equilibrium binding const. toward the optimum binding energy
$B =$ constant correlated to heat of adsorption.

The linearized form of this equation given as follows:

$$q_e = BlnK_T + BlnC_e$$

Linear plot of qe versus *lnCe* was drawn and the values of intercept and slope were calculated. Values of Temkin's constants determined thereafter. Value of KT (equilibrium binding constant) for Cr (VI) and Cd (II) by *A. ferussacianus* was found to be 6.10 and 5.99 respectively, B (Temkin's constant) was 0.98 and 0.85, and R^2 (regression coefficient) was found 0.99 and 0.97 for Cr (VI) and Cd (II) respectively. Figs. 12 and 13

Fig. 10 Freundlich isotherm for sorption of Cr(VI) ion onto *A. ferussacianus* shell

Fig. 11 Freundlich isotherm for sorption of Cd (II) ion onto *A.ferussacianus* shell

Of the various adsorption isotherm modelling employed to the experimental information , Freundlich isotherm was find to be best fitted followed by Temkin isotherm whereas Langmuir isotherm was not found to be fitted as good as the others. Experimental economic values were in agreement with the values obtained from Freundlich isotherm, thus showing multilayer sorption. This finding is in agreement with the previously performed similar subject area [20].

3.7 Kinetic Modeling

Imposter -second parliamentary procedure kinetic model (Ho & McKay, 1999) was employed to evaluate the mechanistic scene of biosorption of heavy metal by using *A. ferussacianus*. Following kinship was used to study Pseudo-second parliamentary law kinetics.

$$\frac{dq_t}{dt} = K_2 (q_e + q_t)^2$$

The above equation could be rearranged to give the following expression:

$$\frac{t}{q_t} = \frac{1}{K_2 \, q_{eq}^2} + \frac{t}{q_{eq}}$$

Where,

t = time (min)
qt = uptake capacity at time 't' (mg/g)
qe = Equilibrium constant of sorbate ion on surface of the biosorbent(mg/g)
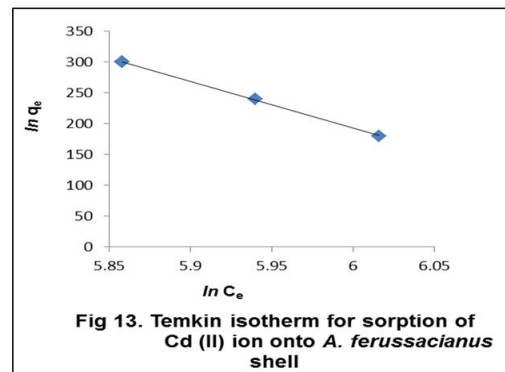K2 = equilibrium rate constant of pseudo-second-order adsorption (g/mg/min)
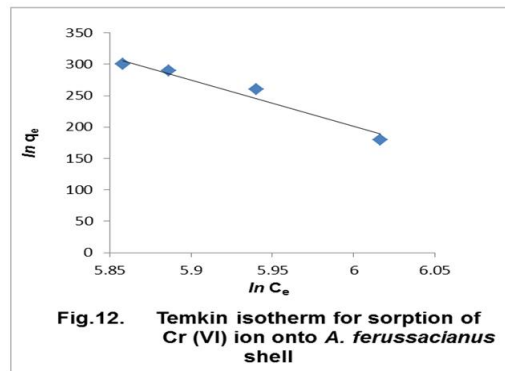

Fig.12.   Temkin isotherm for sorption of Cr (VI) ion onto *A. ferussacianus* shell

Fig 13. Temkin isotherm for sorption of Cd (II) ion onto *A. ferussacianus* shell

Table 1. Values of Cr (VI) and Cd (II) constants of various adsorption isotherms

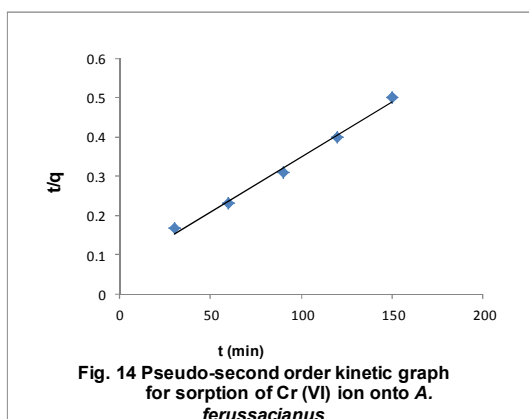| Biosorbent quantity(mg)	Langmuir isotherm constants			Freundlich isotherm constants			Temkin isotherm constants		
	qmax (mg/g)	KL	2R	K	N	KF	R2	KT	B	R2
Cr (VI) Biosorbent quantity (15 mg)	12.06	4.0	0.99	5.70	0.04	1.60	1	6.10	0.98	0.99
Cd (II) Biosorbent quantity (15 mg)	14.04	2.8	0.97	4.94	0.06	1.18	0.99	5.99	0.85	0.97

Table 2. Kinetic constants for Pseudo-second order, the bio-sorption of Cr(VI) and Cd (II) ions by test shell bio-sorbent

Biosorbent	Cr (VI)			Cd (II)		
	q_{eq}	K_F	R^2	q_{eq}	K_F	R^2
A. ferussacianus	2.32	0.19	0.96	5.09	2.40	0.93

Value of equilibrium constant of sobate ion for Cr (VI) & Cd (II) are 2.32 and 5.09 respectively. pseudo-second order 's equilibrium rate constant for adsorption for Cr (VI) and Cd (II) are 0.19 and 2.40 respectively. Regression constant for Cr (VI) and Cd (II) are 0.96 and 0.93 respectively.

Fig. 14 Pseudo-second order kinetic graph for sorption of Cr (VI) ion onto *A. ferussacianus*

Fig. 15 Pseudo-second order kinetic graph for sorption of Cd (II) ion onto *A. ferussacianus*

In Figs. 14 and 15 graphs of kinetic model of Pseudo-second order were found that this model

is not show more result for Cr (II) and Cd (II) by *A. ferussacianus*. The values of Pseudo-second order constants, such as K2, R2, and qeq Cal are revealing normal values. Similar findings have also been reported by the other researchers of biosorption [24].

4. CONCLUSIONS

The ability of the freshwater mussel shell *A. ferussacianus* shell was taken under studied for the eradication of toxic metal ions, such as Cd (II) and Cr (VI). The findings were based on biosorption capacity, equilibrium modeling, kinetic and surface binding sites as observed by FTIR. Experiments were performed as a function of initial solution pH, temperature, initial metal ion concentration, biosorbent dosage and contact time, etc. The solution temperature, pH, and initial metal ion concentration played an important role in affecting the capacity of biosorption. Increase of the pH over 4.0 (in case of divalent Cadmium) and 4.0 (in case of hexavalent Chromium), temperature over 30 degree and initial metal ion concentration of 5 mg/L in Cd (II) and 10 mg/L in Cr (VI) biosorption led to a reduction of the biosorption capacity of the biomass. Optimum biosorbent dosage was 1.5 g/L for Cd (II) ion and 15 mg/L for Cr (VI) ion in the metal ion solution. The equilibrium concentrations of metal ion between the sorbate in the solution and on the biosorbent surface were practically achieved in approximately 90 min (depending on the temperature). Biosorption kinetics was found to follow pseudo-second-order rate expression. Equilibrium biosorption data for all biosorption studies were best represented by Langmuir and Temkin isotherms. The typical dependence of metal ion uptake on

temperature and kinetic studies indicated the biosorption process of *A. ferussacianus* shell for Cd (II) and Cr (VI) ions to be physical adsorption enhanced with chemical effect and diffusion controlled. The present study concludes that *A. ferussacianus* shell may employed as a low-cost and eco-friendly biosorbents as an alternative to the currently used expensive methods of removing toxic metal ions, such as Cd (II) and Cr (VI) from industrial effluents. This may also help in the development of subsequent novel technologies (with better efficiency and eco-friendly) in the application of biosorption at industrial scale.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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