# Utilization of eco-friendly gelatin for Cr(VI) adsorption

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#### ABSTRACT

Gelatin is a biodegradable, biocompatible, non-toxic, non-carcinogenetic and natural polymeric derivative of proteins and peptides. In this article, we applied gelatin as an eco-friendly biosorbent assay for removal of the Cr(VI). The behavior and cogency of gelatin as a biosorbent for interaction with Cr(VI) in aqueous solution was presented. The excellent adsorption properties of gelatin and modified gelatin were confirmed by measuring the capacity of Cr(VI). The batch adsorption model was applied as a function of time, adsorbent dosage, and pH to examine biosorbent's activity. Biosorbents showed an excellent adsorption capacity at pH 3.0. The maximum adsorption capacities was found to be 62.50 and 43.86 mg/g of modified and raw gelatin for Cr(VI) ion respectively. The applicability of Freundlich and Langmuir adsorption models were investigated for Cr(VI)-biosorbent interaction. Equilibrium data followed Langmuir adsorption isotherm excellently.

Keywords: Hexavalent chromium; Gelatin; Equilibrium; Adsorption; Modification

# 1. Introduction

The release of polluting metal ions into the environment by the mining, metal smelting, battery manufacturing, electroplating, electronic, nuclear and other industries contributes a huge burden on environment and contaminate the ground water are the major causes of surface and ground water contamination [1,2]. Out all the heavy metals, Cr(VI) is one of the most significant anthropogenic metal contaminants; and it is easily accumulated in the food chain, which impends human health.

Gelatin is a kind of protein (collagen) that is produced by cow, fish or pig skin and becomes a liquid when heated, and a solid when it cooled. Gelatin have not a distinctive taste and is a solid substance produced in an irreversible hydrolysis reaction and is a natural biopolymer obtained by thermal or physical and chemical denaturation of collagen. It is used commercially as a gelling agent in the production processes of food, pharmaceuticals, photography, and cosmetic ingredients [3]. Gelatin has prominent bioconsistency, biodegradability, non-immunogenicity, and relatively large capacity. It exists in large quantity or supply in nature and it is easily processed into various forms and is an inexpensive material [4–6].

Chromium is widely used in paints and pigments, leather tanning, fungicides, electroplating, cement, steel, ceramic and glass industries [7]. The presence of chromium in the wastewater released by these industries is getting a major interest in the last decade due to its harmful effects on health and environment. Hexavalent chromium ion (Cr(VI)), is a highly oxidizing form of various organic and inorganic compounds.

In general, Cr(VI) ionic forms are anionic in character, such as:  $HCrO_{4^{-}}^{-}CrO_{4^{-}}^{2-}$ , and  $Cr_2O_7^{2^{-}}$  chromate complexes. In addition, Cr(VI) is also known by the US-EPA as well as other agencies as a carcinogenic agent [8]. In other

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words, the most naturally occurring form of chromium is trivalent chromium, Cr(III), which is known to be an essential trace element for some organism [9]. Therefore, such variation between toxicity and nontoxicity of chromium species must manage the interest of scientists toward finding feasible methodology to identify the accurate concentration of each species of chromium with high precision and accuracy rather than determination of the total chromium as can be detected by various instrumental methods [10].

Chemical Sciences are the best way to reduce the chromium compounds released from several industries or turn them into non-toxic forms. Different methods were applied for chromium recovery in wastewater samples and matrices based on various solid phase adsorption approaches. The most important of these methods are; chemical coagulation, filtration, chemical precipitation, ion exchange, adsorption, electro deposition, membrane systems, and the application of membrane technology. All these applied methods have their specific benefits, vast disadvantages and limitations such as incomplete Cr(VI) removal, demands for expensive supplies and monitoring equipment, high reagent, energy requirements or generation of toxic sludge [11–15].

The major objective of this research is to remove Cr(VI) from aqueous solutions on a bio-polymeric matrix composed of gelatin and gelatin-iron(III) oxy-hydroxides in the form of spherical beads. Gelatin obtained from raw hides of cattle and their modified form were used in the adsorption of Cr(VI) experiments. Various reaction parameters such as Cr(VI) ion concentration (250–5000 ppm), initial pH values (1.0–5.0) and biosorbent dosage (0.5–2.5 g) were optimized for efficient adsorption of Cr(VI) dissolved in aqueous medium.

# 2. Experiment

# 2.1. Preparation of solutions and gelatin (GL)

Analytical grade chemicals were used without further purification in the experiments. Various stock solutions were prepared in ultrapure water. The stock Cr(VI) solution with a concentration of 5000 ppm was obtained by dissolving  $K_2Cr_2O_7$  salt (Merck). The GL used in our experiments was obtained from by-products of leather industry.

Beef skin GL powder with an average particle size of 0.1 mm was taken from Kazlı Çeşme Leather Products R&D (Tuzla-Istanbul-Turkey). For the production of GL, cattle hide pieces are subjected to a lengthy treatment with lime and water at ambient temperatures. Depending on treatment, the nature of the beef skin, the size of the pieces, liming is usually 10 weeks in the production plant. The mechanical properties of GL are very sensitive to temperature variations during the production period. For that reason, the temperature dependence of the adsorption was not tried at elevated temperatures. GL were crushed and separated using sieves and shakers with in the size range of 100-200 mesh fractions. The powder was well dried for removing the last traces of moisture at a furnace for one day at 50°C to decrease the water content. Each portion of adsorbent was stored in a desiccator prior to analysis. A typical structure of gelatin unit was given in Fig. 1.

# 2.2. Modification of GL to gelatin-iron(III) oxy-hydroxides (GL-HFO) with ferric nitrate, Fe(NO<sub>2</sub>),

10 g of pre-treated GL was mixed for 48 h with 300 ml of  $0.05 \text{ M Fe}(\text{NO}_3)_3$  in a 1000 mL beaker. Aliquots of sodium hydroxide (1 mol L<sup>-1</sup>) were added drop wise into the beaker from a burette under continuous stirring keeping the pH between 2.8 and 3.5. After 48 h of mixing, the suspension was filtered and the remaining solid was recovered by repeated filtration and washed with ultrapure water in several times until neutral pH. Initially GL-HFO was dried in an oven at 50°C and then was grinded for structural analysis. Then, obtained product was stored in a desiccator at room temperature for further experimental analysis. The pH values of resulting solutions were adjusted by using a calibrated Orion 900S2 Model pH meter. The GL-HFO production process and the adsorption of Cr(VI) is shown in Fig. 2.

#### 2.3. Characterization of the biosorbents

Zeiss LS-10 scanning electron microscopy (SEM) that display the images of biosorbents by scanning it with a focused beam of electrons was employed before and after adsorption of Cr(VI) (Fig. 3). The accelerating voltage was



Fig. 1. A typical structure of gelatin unit (-Ala-Gly-Pro-Arg-Gly-Glu-4Hyp-Gly-Pro-).



Fig. 2. Schematic illustration for the biosorption process.



Fig. 3. The SEM micrograph of (a) GL-HFO (b) GL-HFO/Cr(VI).

a particular shape; and it exhibited a shape such as a small piece of a thin flake (Fig. 3a. and 3b.). The surface morphology of them appears to change significantly following dispersion of Cr(VI) (Fig. 3b). As seen in Fig. 3b, the photograph shows that the porous nature of the outer surface of the biosorbents adsorbed Cr(VI) from the solution.

set to 20 kV with a current 50 pA. The SEM displays the surface morphology of them. The surface morphology and texture of the Cr(VI) loaded biosorbents were completely different compared to the natural ones. A certain change on the powdered beads was observed after the adsorption of Cr(VI). The SEM of GL-HFO and GL-HFO/Cr(VI) formed

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The FT-IR spectra of the chemical compositions of GL and GL-HFO-bound-Cr(VI) were recorded from KBr pellets by using a BRUKER Tensor 37 Fourier transform infrared spectrophotometer in the range of 400–4500 cm<sup>-1</sup>.

Fig. 4a and Fig. 4c represent the FT-IR spectrum of GL-HFO and GL respectively and characterized by the presence of several characteristic peaks that are related to the various functional groups of GL. Bonding of Cr(VI) to the surface of GL was monitored and confirmed from the spectrum (Fig. 4b). GL shows characteristic absorption bands at 1548 cm<sup>-1</sup> (CO stretching band of COO<sup>-</sup> groups) and 1456 cm-1 (COO- symmetric stretching of COO groups). The adsorption bands at 1632, 1510, 1240 cm<sup>-1</sup> are mainly assigned to different types of amide bonds in GL matrix. The peaks around 2964 cm<sup>-1</sup> are related to the symmetric and asymmetric stretching vibration of the aliphatic group (CH<sub>2</sub>) [16]. The 1402 cm<sup>-1</sup> peak was for C-N stretching and 124 cm<sup>-1</sup> peak for N-H bending. A broad peak centred at 3360 cm<sup>-1</sup> is mainly related to the OH group or absorbed water molecules. A characteristic region for Cr(VI) interaction with GL is observed in the frequency region between 900 and 1660 cm<sup>-1</sup>. The difference in the FT-IR spectrum of Fig. 4b reveals that Cr(VI) binds to GL [17]. FTIR characterization mostly confirms various interactions. In this study, the band in the standard spectrum of GL at 1000 cm<sup>-1</sup> disappeared after the interaction of iron with GL. Similarly after modification of GL with iron, this was used further for detection of Cr(VI) ion. The detection of Cr(VI) ion confirmed by slight changes in various bands in the region from 1000-1600 cm<sup>-1</sup>. Disappearance of band and slide shifting of various peaks after interaction of GL-HFO with Cr(VI) confirmed the adsorption phenomena.

#### 2.4. Experimental methods

Various adsorption methods were are effectively applied for adsorption of Cr(VI) by immobilizing to the surface of GL-HFO and used to estimate the capacity factor. The adsorption capacities of biosorbents depend on their porous structure and surface functionality. GL and GL-HFO are new biomaterials to be applied for taking away Cr(VI) in aqueous solution. A *series* of *standard* Cr(VI) solution by

1.05 BRUKER 8 Units 0.95 Absorb 0.90 (b) 1075.95 1240.37 2964.5 (c) 0.85 1402.37 3360.29 8 1632.36 4000 3000 2500 2000 1500 Wavenumber.cm-1

Fig. 4. FT-IR spectra (a) GL-HFO, (b) GL/Cr(VI), (c) GL.

proper dilution of the stock solution were prepared for adsorption experiments.

For the Cr(VI) ion adsorption, a certain amount of biosorbents was brought in to contact with 50 mL of Cr(VI) solution at constant speed using an orbital shaker at 25°C. After filtration, the concentration of Cr(VI) in the filtrate was identified by UV-vis Spectrophotometer (Schmadzu UV-1700) (λ: 540 nm) using a diphenylcarbazide reagent. The total adsorption of Cr(VI) was calculated by taking the difference of initial concentration and total Cr(VI) concentration in the filtrate medium. The effect of the biosorbent dose for the adsorption of Cr(VI) was tried in the batch reactor by varying the biosorbent from 0.5-2.5 g for certain period. The effect of pH on Cr(VI) adsorption was evaluated by controlling the initial pH of the solution within the range of 1–5. The pH of each solution was regulated to the intended value with 0.01 M NaOH and HCl. The solutions in the batch reactor were continuously mixed in the shaker for 6 h. The adsorption of Cr(VI) by the biosorbent is definitely dependent on several parameters; and the major influencing parameters can be expressed in pH, contact time, biosorbent dose, and initial Cr(VI) concentration.

#### 3. Results and discussion

#### 3.1. Effect of contact time

In the concerned experimental work, contact time was varied from 15–1500 min by using GL-HFO for maximum adsorption of Cr(VI). The effect of contact time on the adsorption of Cr(VI) has shown in Fig. 5. During the adsorption phenomena, adsorption of Cr(VI) was steadily increased until the optimum value at equilibrium stage. This figure indicated that the adsorption of Cr(VI) can be considered in two steps: Initially, the adsorption rate is very high in the beginning of the reaction between Cr(VI) and biosorbents in a contact time of 360 min. Secondly, the progress of adsorption was continued slowly until the equilibrium stage.



Fig. 5. Effect of contact time on the adsorption of Cr(VI) by biosorbents. Adsorption conditions; initial concentration of Cr(VI): 2000 ppm, 1.0 g adsorbent, 50 mL solution, temperature:  $25 \pm 1^{\circ}$ C, pH 3.

# 3.2. Effect of solution pH

Effect of the initial pH on the adsorption of the Cr(VI) by the GL and GL-HFO has shown in Fig. 6. In order to find the optimum pH for maximum adsorption efficiency, the experiments were carried out in the pH range 1–5. Because of precipitation of the Cr(VI) ion, at higher pH values were not suitable for the adsorption process. The structural unit of GL is usually composed of (-Ala- Gly-Pro-Arg-Gly-Glu-4Hyp-Gly-Pro-) as shown in Fig. 1. It is mainly based on the presence of some functional and charged groups that are related to the protein side chains. However, certain surface segments of the biosorbents contain either hydrophilic or hydrophobic amino acids [18].

The GL polymer network is highly hydrophilic which absorbs water through hydrogen bonds formed between water molecules and carboxylic acid and amino groups. The maximum adsorption of Cr(VI) on GL-HFO was observed at pH 3 due to the electrostatic attraction of chromate ion (HCrO<sub>4</sub><sup>-</sup>) with protonated amine (NH<sub>3</sub><sup>+</sup>) and surface (FeOH<sub>2</sub><sup>+</sup>) groups on biosorbent surfaces [19].

One of the major important facts about Cr(VI) binding to various functional groups or in the general surface groups is the strong dependency of this process on the pH value of contact solution which favors the direct binding of the Cr(VI) ion to the capturing species. The GL-HFO has the effective functional groups present in the structure such as -OH, -NH<sub>2</sub>, and -COOH. These functional groups play an important role for binding as well as providing active targeted sides for maximum adsorption. In order to account for such a high Cr(VI) adsorption capacity value, the possibility of ion-ion interaction and of the binding of negatively charged hexavalent chromium forms (HCrO<sub>4</sub><sup>-</sup> or CrO<sub>4</sub><sup>2-</sup>) to the positively charged quaternary ammonium groups on the surface of GL biosorbents in the acidic pH region can be considered [20]. In low pH values (pH 1.0 and 2.0), the number of protons from aqueous solution is high and most of the functional groups on the biosorbent surface are not dissociated. The Cr(VI) in this case can interact with some functional groups on the biosorbent surface.

The chromate may be presented clearly in various forms such as  $H_2CrO_4$ ,  $HCrO_4^-$ ,  $Cr_2O_7^{2-}$ ,  $CrO_4^{2-}$  in the bulk phase as a function of pH and concentration. Only  $CrO_4^{2-}$  ions appear in the solution when pH > 6.5; in the pH range from 0 to



Fig. 6. Effect of pH on the adsorption of Cr(VI) using the biosorbents. Adsorption conditions; initial concentration of Cr(VI): 2000 ppm, 1 g adsorbent, 50 mL of solution, temperature:  $25 \pm 1^{\circ}$ C, contact time: 360 min, pH = 1–5.

6.5,  $HCrO_4^-$  and  $Cr_2O_7^{2-}$  are predominant [17]. At the lower pH values of the studied range, i.e. 1-3, the suspension was highly acidic in nature and the bio-polymeric beads contained positively charged groups such as -NH<sup>+</sup> and -NH<sup>+</sup>, etc. due to GL. At this pH, the solution majorly contains  $Cr_2O_7^{2-}$  ions and relatively lesser number of HCrO<sub>4</sub> ions. Now, as the pH is increased in the range 3.0–5.0, there is a gradual conversion of  $Cr_2O_7^{2-}$  ions into  $HCrO_4^{-}$  ions and at the same time, positive charge goes on decreasing while negative charges continuous to increase on the GL molecules. Thus, a greater number of HCrO<sub>4</sub><sup>-</sup> ions get adsorbed by negative sites via H-bonding then onto positive sites via electrostatic binding. This explains a constant rise in the adsorption of Cr(VI) with increasing pH until pH 3. However, at higher pH value greater than 5, the net charge on GL macromolecules becomes negative; and at the same time, the solution only contains  $Cr \bar{O}_{\scriptscriptstyle\!4}^{2\text{-}}$  ions. This obviously results in an enhanced repulsion between the GL and anionic species and thus represents a decreasing adsorption.

Fig. 6 is a representation for the effect of pH on the biosorption percentage values of Cr(VI) by GL. As the pH is increased in the range 3.0-5.0, there is a gradual conversion of  $Cr_2O_7^{2-}$  ions into  $HCrO_4^{-}$  ions and at the same time positive charge goes on decreasing while negative charges goes on increasing on the GL molecules. An adsorption phenomenon is mostly dependent on pH values of aqueous solutions. At the beginning of the equilibrium investigation state, pH of the metal solution was adjusted by optimizing within acidic pH range. In concerned study, initial pH was studied from 1-5. Maximum adsorption was found at pH 3 as expressed in Fig. 6. Various acidic and basic solutions required a suitable pH for the specific interactions. At a particular pH surfaces became more activated and provides specific route for sensing of various ions. Interaction of GL-HFO with Cr(VI) ion require a suitable pH for maximum adsorption of Cr(VI) on the surface of GL-HFO. Therefore, we optimized the pH and concluded that at pH 3, GL-HFO provided maximum adsorption capacity on surface for detection of Cr(VI) ion. GL is highly soluble within the range of 1-2 pH values. When the pH of Cr(VI) solution become lower than 2, GL will be more soluble and the adsorbent sides on the surface of GL became limited. For that reason at lower pH values, minimum adsorption of Cr(VI) was observed in the conducted experiment.

GL, because of its amphoteric nature possesses both positive and negative charged centres due to its isoelectric point and pH of the environment. Thus, depending on the nature of the toxic metal ion an optimum adsorption can be succeeded by a proper adjustment of the pH of the solution. The zeta potential of the biosorbents shows that in a basic medium, the biosorbents' surface exhibited a negative potential due to the formation of FeO-. In the acidic medium, the carboxylic and amine groups will be protonated. In this regards, both amine and carboxylic groups also play and important role in adsorption of Cr(VI) because, they have also charges on their surfaces. The surface also depends on pH, as the pH become acidic, the surface is positively charged and in basic regions surfaces became negatively charged. So, in conclusion, amine and carboxylic groups of GL also contribute in adsorption of Cr(VI). However, when put into an acidic medium, the positive surface charge prevailed due to the formation of FeOH<sup>2+</sup>.

Electrostatic attraction between the positively charged surface hydroxyl groups  $FeOH^{2+}$  and negatively charged chromium species (HCrO<sub>4</sub><sup>-</sup>) was responsible for the adsorption of Cr(VI). Thus, greater number of HCrO<sub>4</sub><sup>-</sup> ions was adsorbed onto negative sites via H-bonding and onto positive sites via electrostatic binding. This obviously explains a constant rise in the adsorption of Cr(VI) with increasing pH [21]. The adsorption of Cr(VI) with the biosorbents increased on the small scale with the increase in pH from 1 to 3. Beyond pH 3.2, there is sudden decrease in Cr(VI) adsorption for the biosorbents. For both of the biosorbents, the optimum pH was preferred as 3.0.

### 3.3. Adsorption isotherms

Equilibrium studies which give the capacity of the biosorbents and sorbates are performed with the adsorption isotherm which is usually the relation between the quantity adsorbed and the amount of Cr(VI) staying in the solution phase at a certain temperature at equilibrium.

The equilibrium adsorption isotherm is a fundamental and essential procedure for describing the possible interactive trends between the two interacting species (adsorbates and biosorbents). To investigate  $q_e$  as a function of ion concentration, different adsorption isotherms (Langmuir and Freundlich isotherm), were used to obtain experimental data. The mechanism for the interaction of Cr(VI) on the biosorbent site was based on the adsorption isotherms. It was characterized by certain constants which supplies information about the surface properties and the affinity of biosorbent toward Cr(VI) in the solution phase. In this study, a non-linear method of widely used isotherms, and the adsorption data of the Cr(VI) ion were correlated with Langmuir and Freundlich models [Eqs. (1) and (2)] [22,23].

Langmuir equation [Eq. (1)]:

$$\frac{C_e}{q_e} = \frac{1}{K_b A_S} + \frac{C_e}{A_S} \tag{1}$$

where  $A_s$  and  $K_b$  are coefficients,  $q_e$  is the weight adsorbed Cr(VI) ion per unit weight of biosorbent and  $C_e$  is the Cr(VI) ion concentration in bulk solution at equilibrium.

Freundlich equation [Eq. (2)]:

$$q = K_f C_e^n \tag{2}$$

where *n* is the Freundlich constant, and  $K_f$  is the adsorption coefficient, *q* is the weight of the adsorbed Cr(VI) ion per unit weight of sorbent, and  $C_e$  is the equilibrium for the Cr(VI) concentration in bulk solution. Log scale was taken; and equation rearrangements (2) were made.

$$\log q = \log K_f + n \log C_e \tag{3}$$

The adsorption of Cr(VI) ions was observed at different initial chromium concentrations ranging from 250 to 5000 ppm, at pH 3 with the optimum agitation speed and period (Fig. 7). These isotherms relate Cr(VI) adsorption per unit weight of resin  $q_e$  to the equilibrium Cr(VI) concentration in the bulk fluid phase  $C_e$ . The Langmuir equation was more applicable than the Freundlich equation although both described the adsorption data adequately. The linear



Fig. 7. Adsorption isotherm of Cr(VI) ion on GL and GL-HFO as a function of initial Cr(VI) concentration (250–5000 ppm) and 50 mL of Cr(VI) solution at pH 3.0; 1 g adsorbent, temperature:  $25 \pm 1^{\circ}$ C, contact time: 360 min.

plots of  $C_{eq}/q$  vs  $C_{eq}$  show that the adsorption follows the Langmuir adsorption model. The Langmuir model fit well in the pH range of 2.2–3.0. The correlation coefficients are calculated as 0.99 and the maximum adsorption capacities are found as 43.86 and 62.50 mg per g of GL and GL-HFO for Cr (VI) ion, respectively from Table 1.

The essential characteristics of the Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter ( $R_L$ ), which is defined as follows

$$R_{I} = 1/(1 + K_{L}C_{e}) \tag{4}$$

where  $C_e$  is the initial concentration of Cr(VI). The  $R_L$  value indicates the shape of isotherm, which predicts whether an adsorption system is favorable or unfavorable. The calculated  $R_L$  values were between 0 and 1, which indicated a favorable adsorption and these confirmed that the biosorbent were suitable appliers for Cr(VI) adsorption.  $R_L$  was calculated as 0.263 and 0.151 of GL and GL-HFO respectively for the equilibrium and provided the required conditions.

The  $NH_2$  functional groups in the chemical structure of GL reacted with Fe from iron oxide is given in Eq. (5).

$$X.....NH_2 + Fe \rightarrow X....NH-Fe + Cr(VI) \rightarrow [X....NH-Fe]Cr(VI) (Adsorption) (5)$$

Table 1

Freundlich and Langmuir adsorption isotherm parameters

Adsorbent	Langmuir			Freundlich		
	$q_{max}(mg/mg)$	$K_L$ (I/mg)	$R^2$	п	$K_{f}$	$R^2$
Gelatin	43.86	0.0014	0.99	2.5	1.44	0.87
Gelatin-Fe	62.50	0.0028	0.99	3.6	6.10	0.91

GL released one hydrogen atom from amide functionality and provided the chemical reaction to Fe. Further, the complex structure with Fe adsorbs Cr(VI) on the exposed surface which is suitable for adsorption of Cr(VI). Cr(VI) anions are poorly adsorbed at higher pH than at low pH through repulsive electrostatic interactions. At low pH, – NH<sub>2</sub> groups of GL get protonated and the high adsorption capacity of Cr(VI) ions can be expected by the electrostatic attraction between the negatively charged chromate anion and the protonated –NH<sub>2</sub> groups.

#### 3.4. Effect of biosorbent dose on the adsorption Cr(VI)

The selected doses of GL and modified GL was 0.5, 1.0, 1.5, 2.0 and 2.5 g, while the concentration of Cr(VI) was hold constant throughout the adsorption equilibrium and the results are compiled in Fig. 8.

The results in Fig. 8 show that the retention of Cr(VI) increased with the increase of the biosorbent dose up to 1.0 g. After that, it decreased. It is readily understood that the number of available adsorption sites increases with the increase of the biosorbent dose. But, beyond a certain value of the dose amount, the adsorption efficiency of Cr(VI) ion decreased. The decrease in adsorption density is due to the fact that some of the adsorption sites stay unsaturated during the adsorption process. Whereas, the number of available sites on the biosorbent increases as the biosorbent dose increases and this results in an increase in adsorption percentage.

When the increase in amount of dosage of GL, the adsorption capacity increases, but in our study the adsorption capacity decreases due to the steric effects that hindered the efficiency of Cr(VI) adsorption. It is readily understood that the number of available uptake sites increases with the increase of the biosorbent dose. But, beyond a certain value of the dose amount, the adsorption efficiency of Cr (VI) ion decreased. The decrease in adsorption density is due to the fact that some of the uptake sites stay unsaturated during the uptake process.

# 4. Conclusion

The adsorption of Cr(VI) increased with an increase of contact time and attained an optimum at about 360 min for



Fig. 8. Effect of biosorbent dose on the adsorption of Cr(VI). Adsorption conditions; initial concentration of Cr(VI): 2000 ppm, 0.5-2.5 g adsorbent: 50 mL of solution, temperature:  $25 \pm 1^{\circ}$ C, pH 3, contact time: 360 min.

GL and GL-HFO. Cr(VI) was appreciatively adsorbed by GL-HFO in pH range 2.2–3.0. Various models were applied during study. The maximum adsorption capacity of Cr(VI) in solution was achieved at pH 3.0. Further, the adsorption study of Cr(VI) showed that, it obeys Langmuir isotherm model. The most important value obtained from the use of Langmuir model is the  $q_{max}$  value which was found to be 43.86 and 62.50 mg per g of GL and GL-HFO, respectively.

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