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Biosorption of hexavalent chromium using biofilm of *E. coli* supported on granulated activated carbon

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Abstract The optimization of hexavalent chromium biosorption has been studied by using three different biosorbents; biofilm of *E. coli* ASU 7 supported on granulated activated carbon (GAC), lyophilized cells of *E. coli* ASU 7 and granulated activated carbon. Supporting of bacteria on activated carbon decreased both the porosity and surface area of the GAC. Significant decrement of surface area was correlated to the blocking of microspores as a result of the various additional loads. The experimental data of adsorption was fitted towards the models postulated by Langmuir and Freundlich and their corresponding equations. The maximum biosorption capacity for hexavalent chromium using biofilm, GAC and *E. coli* ASU 7 were 97.70, 90.70, 64.36 mg metal/g at pH 2.0, respectively. Biosorption mechanism was related mainly to the ionic interaction and complex formation. Based on the experimental conditions, the presence of bacteria could be enhanced the capacity of activated carbon to adsorb hexavalent chromium ions from aqueous solutions.

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Introduction

Chromium is one of the most widely used metals in industry (Zemin et al. 2007) since it is an essential trace element for all living organisms. The common oxidation states of chromium are the trivalent and the hexavalent forms (Tunali et al. 2006). Hexavalent chromium has been recognized as one of the most dangerous environmental pollutants due to its ability to cause mutations, irritation, corrosion of the skin and respiratory tract to humans. It also causes lung carcinoma in humans (Liu et al. 2006; Ganguli and Tripathi 2002; Bhinde et al. 1996). Removal of heavy metals from wastewater is usually achieved by physical and chemical processes which include precipitation, coagulation, reduction, membrane processes, ion exchange and adsorption (Lameiras et al. 2008; Trivedi and Patel 2007). However, the application of these techniques to lower metal concentration in wastewater is sometimes restricted, due to technological or economical reasons. The scientific search for novel technologies has been directed to the application of biosorption processes. The latter consist of several mechanisms, mainly ion exchange, chelation, adsorption and diffusion through cell walls (Ganguli and Tripathi 2002; Lameiras et al. 2008). Another promising technology is used in removing of heavy metals is a bacterial biofilm supported on granular activated carbon (GAC). Granular activated carbon filters are used on a

final polishing step in drinking water in order to remove compounds that are usually present in the water at low concentrations (algal toxins, pesticides, taste odours and industrial micro pollutants) (Snyder et al. 1995). Biofilms can be defined as communities of microorganisms attached to a surface (Quintelas et al. 2007). The biofilm formed on the GAC changes the surface charge density of the activated carbon, which mainly directed to increase its negative charge value, which could enhance its adsorption capacity against some positively charged pollutant species, such as most of the heavy metals (Rivera-Utrilla et al. 2001). The use of a biosorption system consisting of a biofilm supported on GAC combines the ability of the biofilm to remove heavy metals with the ability of the activated carbon to remove organic compounds (Scott and Karanjkar 1995).

The main objective of this study is to follow the biosorption of hexavalent chromium on biofilm of *Escherichia coli* ASU 7 and GAC, GAC and *E. coli* ASU 7. Characterization of the different biofilms was performed in order to select the most efficient biosorbent.

Materials and methods

Biosorbents and their preparation for biosorption

The bacterial strain used in the present study was *E. coli* ASU 7, isolated from metal polluted wastewater of mining activities in Assiut, Egypt. It was isolated by using *E. coli* broth (Atlas 2004) and found that it is highly tolerated to hexavalent chromium. In this study we have three different biosorbents: Bacteria, granulated activated carbon and biofilm.

Bacteria

E. coli ASU 7 strain was inoculated in nutrient broth medium Atlas (2004) at 37°C with agitation 150 rpm on a shaker for 24 h then centrifuged to recover the cells; the pellet was washed three times with sterile deionized water, finally cells were lyophilized using lyophilizer (#6KBTES-55Virtis, USA).

GAC

GAC was obtained from (ADWIC) company, Egypt. It was characterized by highly surface area 1,548.37 m²/g and a total pore volume of 1.299 cc listed as in Table 1.

Biofilm

Biofilm was prepared using different weights of bacteria (0.5, 1, 1.5, 3 g) loaded on the surface of granulated activated carbon (1 g). The biofilm was prepared by two different methods.

Table 1 Texture data obtained from nitrogen adsorption at −196°C, samples 1–4 represent biofilm (1 g activated carbon with different weights of 0.5, 1, 1.5, and 3 g bacteria), respectively, prepared by first method; samples 5–8 represent biofilm (1 g activated carbon with 0.5, 1, 1.5, and 3 g bacteria), respectively, prepared by second method; sample 9 represent activated carbon; sample 10 represent lyophilized bacteria

Sample	S_{BET} (m²/g)	r_p (Å)	V_P cc
1	567.06	3.45	0.489
2	386.14	3.43	0.331
3	163.18	3.93	0.160
4	34.56	5.48	0.047
5	793.24	3.31	0.656
6	595.89	3.39	0.505
7	670.64	3.43	0.575
8	303.04	4.17	0.316
9	1,548.37	3.35	1.299
10	0.811	–	–

V_p, total pore volume expressed in cc; r_p, pore diameter expressed in Å; S_{BET}, specifies surface area (m²/g)

First method (shaking method) Activated carbon and bacteria were mixed in sterilized deionized water and incubated in a shaker at 37°C for 72 h then centrifuged, the supernatant was decanted and the pellet was dried in drying oven at 50°C over night to insure drying (Rivera-Utrilla et al. 2001).

Second method (impregnation) This method was used for the first time with bacteria; granulated activated carbon was mixed with bacteria by impregnation. The required amounts of GAC and bacteria were weighted to the nearest milligram. The impregnation procedure applied was similar to that detailed else where (Myers and Lunsford 1985; Kugel et al. 1975). The impregnated solution was prepared by suspending the calculated amount from both GAC and bacteria in a suitable volume of sterilized deionized water. Evaporation of the excess water was done by drying on a water bath at 100°C, and then the pellet was dried in the oven at 50°C over night till constant weight (moisture content ≈ 0). The biofilm prepared by impregnation was chosen for all adsorption experiments, since the adsorption capacity and texture properties of this biofilm was expected to be efficient than that prepared by shaking.

Characterization of biosorbents

Surface area measurements and texture properties

The textural properties of different biosorbents were determined from their adsorption–desorption isotherms of liquid nitrogen at 77 K using ASAP 2010 software. The

surface and texture properties of all absorbent samples have been assessed by measuring the nitrogen adsorption isotherm at −196°C. The specific surface area was evaluated by applying the Brunauer Emmer and Teller (BET) method (Brunauer et al. 1938), pore size and pore volume data were obtained by the Barrett–Joyner–Halenda (BJH) method (Barrett et al. 1951). All samples were degassed at 80°C for 1 h in nitrogen atmosphere prior to any adsorption process.

Infrared analysis

Infrared spectroscopic analysis for the samples under investigation was performed in order to give a qualitative and preliminary characterization of the main functional chemical groups present on the bacterial biomass which are responsible for heavy metal biosorption. A raw sample of bacterial biomass and biomass loaded with Cr^{6+} were analyzed using an Infrared spectrophotometer (IR) Model 470 Shimadzu corporation adopting KBr disk technique (Schwarz et al. 1985).

Preparation of metal solutions

Stock solution (1,000 ppm) of Cr^{6+} was prepared by dissolving analytical grade of $K_2 CrO_4$, in distilled water. Before mixing with the biosorbents, the stock solution was diluted to the required concentration.

Effect of pH on biosorption

The impact of the solution pH on the metal biosorption was investigated in the different biosorbents and conducted at different pH environment (ranging from 2.0–7.0) containing 20 ml of metal solution. The pH adjustment was done with the addition of either 0.1M NaOH or 0.1M HCl. Sodium nitrate (0.1M) was used as a supporting electrolyte for all experiments.

Effect of contact time on biosorption

Experiments for determining the equilibrium time needed for biosorption process were performed using 50 mg from the initial metal concentrations of Cr^{6+} ions, in 20 ml of metal solution at pH 2.0 and at room temperature. Metal solutions were taken at the desired intervals from (0 to 60 min) and were subsequently centrifuged at 10,000 rpm for 5 min. The heavy metal concentration in the resulting supernatant was determined by atomic absorption spectroscopy (AAS) Model 210 VGP Buck Scientific.

Adsorption experiments

In this study, the biosorption isotherms of the Cr^{6+} ions were obtained at pH's of 2.0. The sorption experiments were carried out using 20 mg from each biosorbent in conjunction with the concentration of Cr^{6+} starting from 0 to 150 ppm and 20 ml of deionized water. Shaking was affected at 200 rpm for 30 min till equilibrium attained. Experiments were conducted at room temperature (30 ± 2°C). Then the samples were centrifuged at 10,000 rpm for 5 min and the heavy metal concentration in supernatants was measured by AAS.

Data evaluations

The amount of metal adsorbed by bacterial biomass was calculated from the differences between the metal quantity added to the biomass and the metal content of the supernatant using the following equation:

$$q_{eq}(mg/g) = \left[\frac{C_i - C_e}{M}\right] \times V \tag{1}$$

where q_{eq} is the amount adsorbed at equilibrium, C_0 and C_e are the initial and equilibrium concentrations (the solution concentration at the end of the sorption process (mg/l), V the volume of solution (l), m the weight of biomass in grams.

Results and discussion

E. coli ASU 7 biomass characterizations

Infrared analysis

Figure 1 represents IR spectrum for the control sample. The absorption bands characterizing hydroxyl and amino groups were assigned at 3,276 cm^{-1}, alkyl chains have a broad band within the range 2,921–2,851 cm^{-1}, C=O of amide groups are assigned at 1,648 cm^{-1}, COO$^-$ of the carboxylate groups appeared at 1,544 cm^{-1}. The band located at 1,398 cm^{-1} is an indication of the presence of COO$^-$ anions where that located at 1,238 cm^{-1} was assigned to SO$_3^-$ groups.

Moreover the bands located at 1,034 and 1,075 cm^{-1} were attributed to the organic phosphate groups and to the P–O of the (C–PO$_2^{-3}$) moiety, respectively. On the other hand, the band appeared at 726 cm^{-1} was attributed to the S–O link of the (C–SO^{-3}) groups. The IR spectrum of Cr^{6+} loaded biomass is shown in (Fig. 1b). A trial to compare between the spectrums of native biomass with that found in case of metal loaded, one can revealed the following:

Fig. 1 IR analysis for the biomass before biosorption (**a**), **b** after 60 ppm Cr^{6+} biosorption
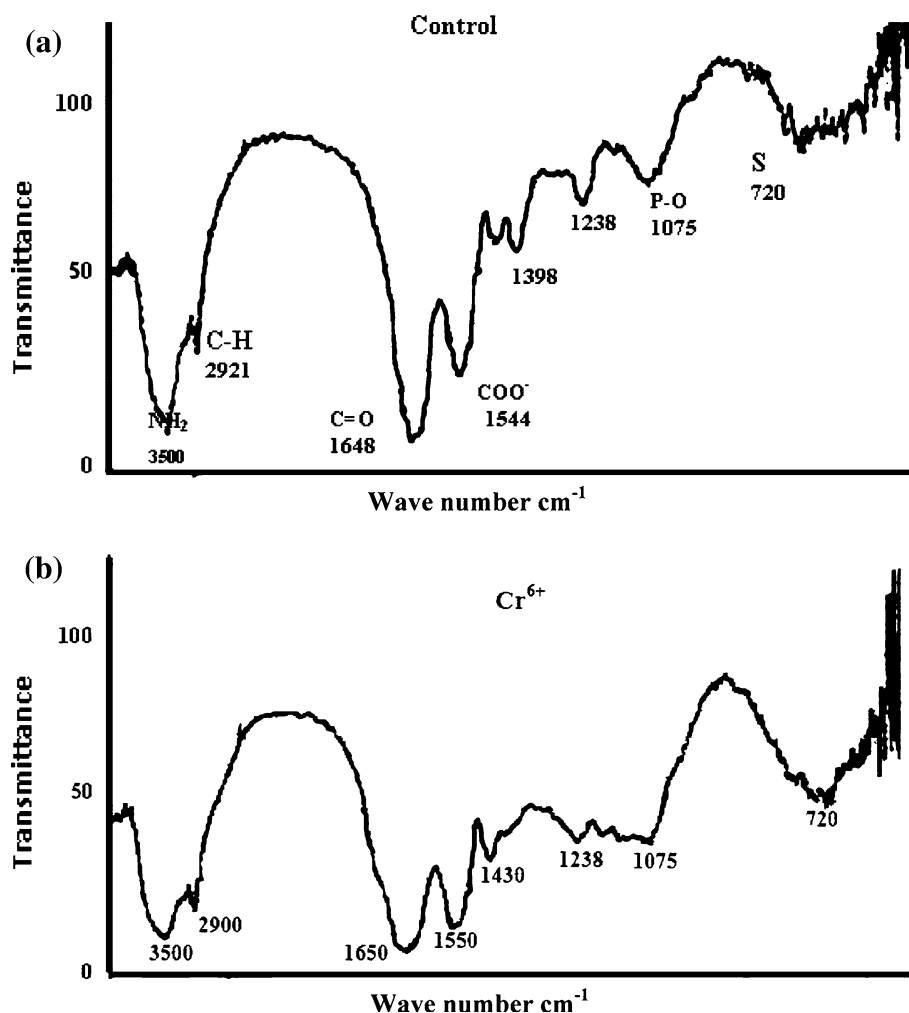
(1) Broadening of the band characterizing the presence of C=O groups was observed at range of 1,650–1,660 cm^{-1}, a thing that indicates the interaction of Cr^{6+} with C=O groups on the surface of the biomass (2) shifting and broadening of the bands located at 1,544 to 1,550–1,555 and that at 1,398–1,420 cm^{-1} were anticipated to the loading affect of Cr^{6+}. In addition these broadening were explained by the involvement of H-bonding (Sar et al. 1999). (3) The disappearance of the band appeared at 1,075 cm^{-1} was attributed to the blocking affect of Cr^{6+} as a result of the interaction of such sorbed ions with the phosphate groups. Additionally (4) the bands located in the range 3,500–3,600 cm^{-1} were verified the interaction that takes place on both the hydroxyl and amine groups. These bands became more intense and broad after the reaction takes place indicating the formation of more OH^- groups by Cr^{6+} reduction. Finally the bands at 1,550, 1,555, and 1,560 cm^{-1} became broad after adsorption take place on carboxyl.

The above observations indicate the involvement of these functional groups in biosorption process. These results are in a good agreement with those obtained by (Lameiras et al. 2008; Lodeiro et al. 2006; Komy et al. 2006; Tunali et al. 2006; EL-Shafey 2005) they come to the conclusion that the main functional groups responsible for biosorption of heavy metals were carboxylic, hydroxyl and amino groups.

Textural characteristics

All the isotherms displayed type III, in the IUPAC classification (Sing et al. 1985) indicating the micropores nature of the different adsorbents. Also the curves indicating that all samples exhibit microporous character with a rather significant hysterysis loop of H_3 type closing within the range of (P/P_0) 0.4–0.6, which denoting the presence of aggregates of plate like particles giving rise to slit shaped pores (Lecloux and Pirard 1979). The specific surface area were determined using the BET equation and were given in Table 1.

The microporosity is further confirmed from analysis of the V_a–T plots given in Fig. 2, which lead in all cases to
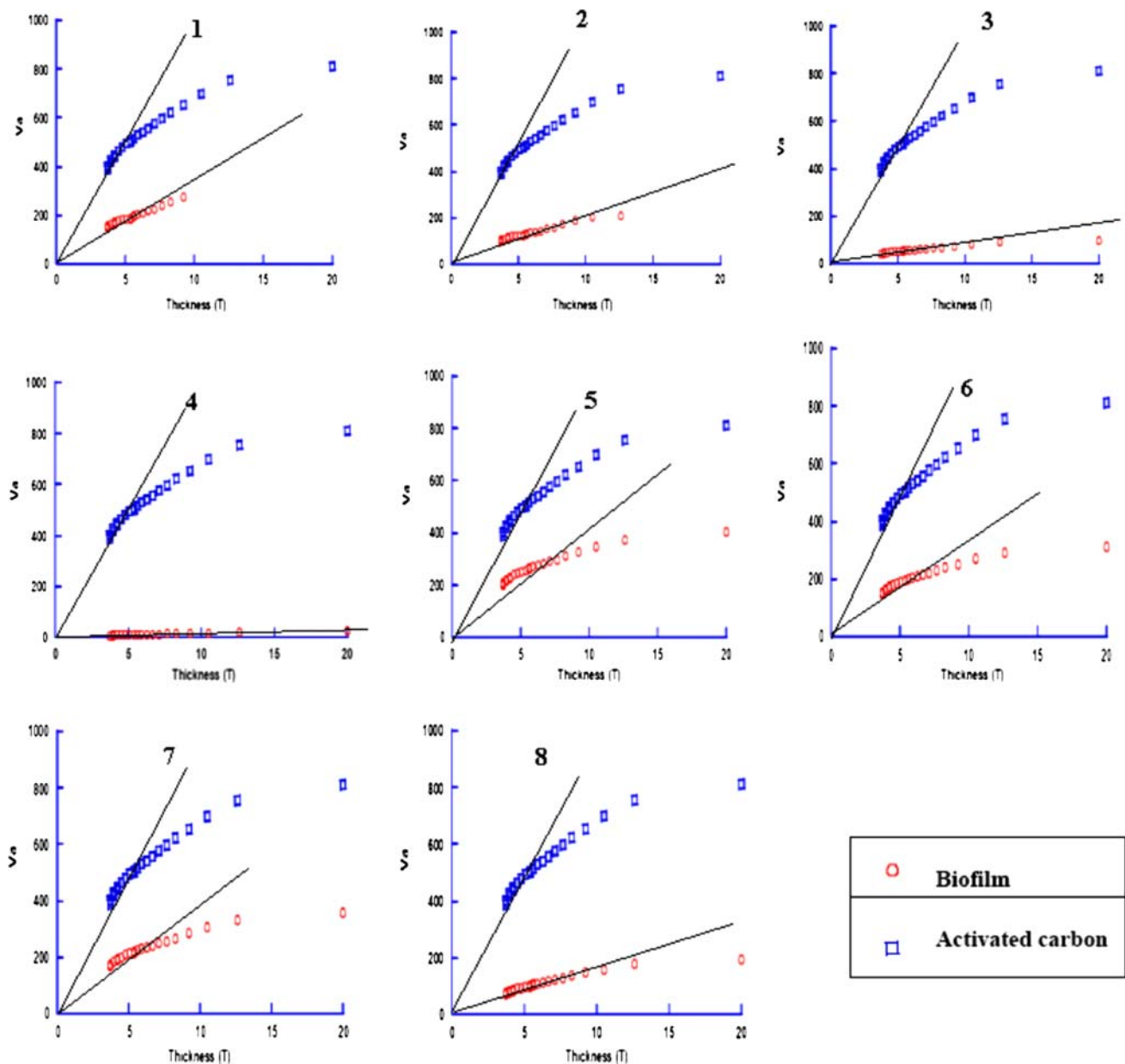
Fig. 2 The V_a–T plot obtained upon analysis of the adsorption isotherm, where V_a is volume of adsorbed nitrogen (V_a) in cc and T is the thickness of layers in Å. *Sample 1–4* represent biofilm (1 g activated carbon with different weights of 0.5, 1, 1.5, and 3 g bacteria), respectively, prepared by first method; *Sample 5–8* represent biofilm (1 g activated carbon with 0.5, 1, 1.5, and 3 g bacteria) (○), respectively, prepared by second method. All samples contain activated carbon (◇)

straight lines passing the origin at low values of P/P_0 and show a downward deviation start at higher P/P_0 values which are consistent with those at which closure of hysterysis loop are taken place.

The S_{BET} values together with the total pore volume and average pores diameter are summarized in Table 1. The value of average pore diameter indicates also that range of pore size is assigned to be microporous in nature. However, the marked decrease in the average pore diameter and consequently the significant decrease in the specific surface area are most probably due to the blocking of the

micropores as a result of the addition of bacteria with different loads. Therefore this would lead to a structure of interanueller region that gives rise to sub-blocking of the pores. Furthermore, the decrease in the total pores volume with increasing the percentage loading of bacteria can also be interpreted in a similar manner given above when we are discussing the variation in both S_{BET} values and the pore diameter characterizing the different samples.

Pores size distribution (PSD) curves reveal a major contribution of a peak laying within the microporous range for all samples under investigation. However, the pore size

distribution (PSD) curves for the treated samples show a bidesperse character in comparison to those correspond to non-treated activated carbon curves. Such behavior indicates the blocking affect of bacteria of the already present pores in the activated carbon surface as a result of penetration and occupation of these species in large fractions of pores.

Effect of pH

The pH of the metal solution plays a crucial role in the passive microbial biosorption (Pardo et al. 2003). Moreover, it has been shown that the affinity of anionic species towards the functional groups present in the cellular surface is strongly affected by the pH value (Schiewer and Volesky 1995). Figure 3 summarizes the adsorption results of Cr^{6+} ions of different biosorbents as a function of pH. These results indicate that, optimal pH value for Cr^{6+} biosorption is 2.0.

From IR studies, it became clear that the cell wall contains amines, amides, and carboxylic functional groups that are protonated, depending on the pH of the aqueous medium. Anions could be expected to interact more strongly with cells as the concentration of positive charges increases. A fact which shows a shift in biosorption maxima at lower initial pH values upon increasing the hexavalent concentration. Such increase is attributed to the protonation process of functional groups at low pH values (Lopez et al. 2001). Cr(VI) and some other metals known

to be exist as anions, depending on the pH of solution and this means that the adsorption of Cr(VI) was favourable at low pH. In our results we found that optimum pH for Cr(VI) biosorption is 2.0. At low pH values, cell wall functional groups are protonated and compete significantly with metal binding. As the pH increased further, the overall surface charge on the cells could become negative and biosorption decreased. This results also agrees with previous studies of Cr(VI) biosorption by different biosorbents (Khambhaty et al. 2009; Bai and Abraham 2001; Park et al. 2005; Tewari et al. 2005).

Furthermore, our results are in agreement with many investigators, EL-Shafey (2005) stated that the optimal pH for Cr(VI) sorption using rice husk was in the pH range 2.0–2.8. Sharma and Forster (1996), in their study, found that sorption maximum lies in the range of pH 2.5–3.0. Similarly Mise and Shantha (1993a, b) noted that the higher Cr(VI) uptake was achieved at pH 2.0 using activated carbon. On the other hand, Sharma and Forster (1993) found that the maximum uptake of Cr(VI) is located in the range of pH 1.5–3.0 using Sphagnum moss peat while in using saw dust sorbent, the optimal pH range for sorption is 2.0–3.0 (Sharma and Forster 1994).

Effect of time on biosorption

The quantitative measurements of metal uptake by biosorption were plotted against time at the characteristic optimum pH values. Figure 4 showed that the rate of metal uptake increases rapidly in the first part within 5 min of contact. After that the rate decreases till we reach a constant value of metal concentration after 30 min. Therefore, one can conclude that the appropriate equilibrium time for measurements found to be at 30 min. This short time required for biosorption is in accordance with the result given by other authors (Gabr et al. 2008; Komy et al. 2006; Tunali et al. 2006; Akar and Tunali 2005; EL-Shafey 2005; Pardo et al. 2003; Ganguli and Tripathi 2002) they reported that the contact time for complete biosorption in the same order of magnitude for similar biomass. In our case, a reaction time of 30 min was selected to ensure an optimum metal uptake.

Langmuir adsorption isotherm

Sorption performance of hexavalent chromium ion on different biosorbents was achieved by the biosorption equilibrium measurements using initial concentrations within the range of 0–150 mg/l at 30 min and at pH of 2.0 as in Fig. 5. Equilibrium sorption studies revealed that metal biosorption proceed through chemically equilibrated and saturable mechanism. Thus, there was an increase in metal uptake as long as binding sites were free. When the
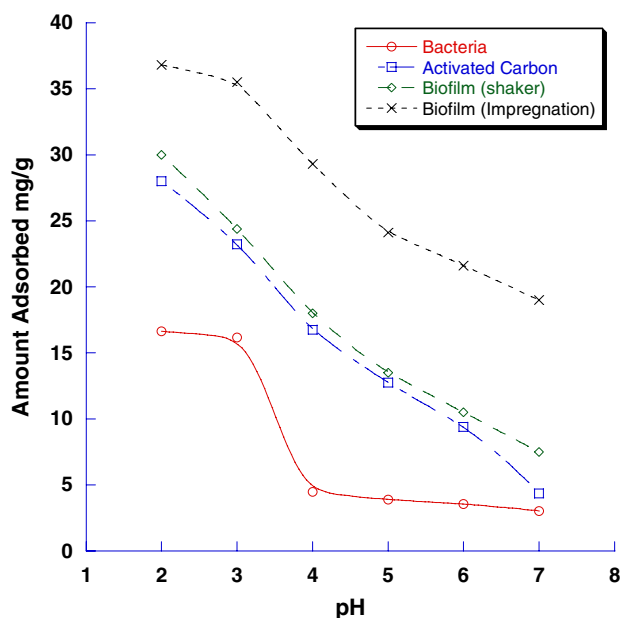

Fig. 3 Effect of different pH's on Cr^{6+} biosorption by Biofilm (◇), activated carbon (□) and biomass of resistant strain *E. coli* ASU 7 (o) at 30°C, and 30 min
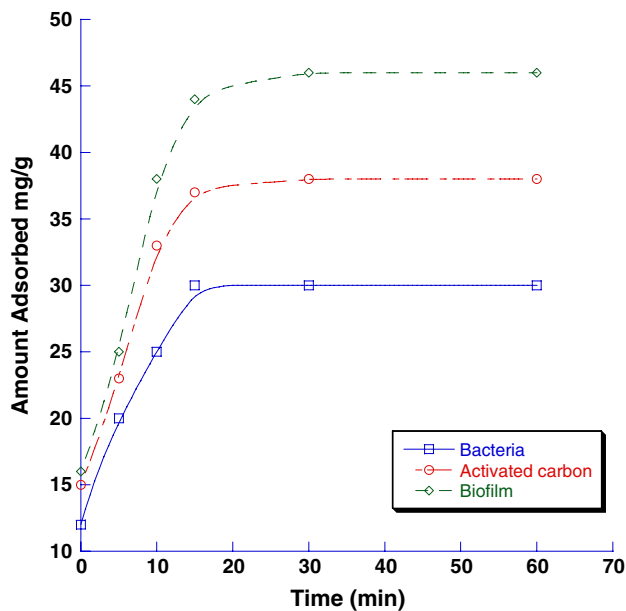
Fig. 4 Effect of time on Cr^{6+} biosorption by Biofilm ($\diamond$), activated carbon (o) and biomass of resistant strain *E. coli* ASU 7 ($\square$) at 30°C and pH 2

Fig. 5 Adsorption isotherm of hexavalent chromium by Biofilm ($\diamond$), activated carbon (o) and biomass of resistant strain *E. coli* ASU 7 ($\square$) at 30°C, pH 2 and equilibrium time at 30 min

experimental data were applied to adsorption models such as Langmuir, equation having the formula:

$$q_{eq} = \frac{q_{max} b C_e}{1 + b C_e} \qquad (2)$$

and its linear form

$$C_{eq}/q = 1/q_{max}b + C_{eq}/q_{max} \qquad (3)$$

where q_{max} is the Langmuir constant (mg/g) which reflects the maximum adsorption capacity, the Langmuir constant b (l/mg), was ascribed to the ratio between adsorption rate constant and desorption rate one. This constant also gives a management of an indication to the affinity of the metal towards the binding sites present on the biosorbent surface (Volesky and Holan 1995; Chong and Volesky 1995).

The Langmuir model is usually served to estimate the maximum metal uptake values (q_{max}) that can be reached in the experiments. Validity of these data through the Langmuir model indicates that the experimental results are fitted well with Langmuir equation (r^2 0.98) than Freundlish model (r^2 0.92) and the biosorption of metal in the present study can be characterized by a monolayer formation of the metal ion on the surface of biomass. Moreover, it is belongs to a single type phenomenon with no interactions between sorbed metals (Langmuir 1918). Linear transformation of the data using the linear form of Langmuir Eq. 3 was expressed in Fig. 6. Values of Langmuir parameters are summarized in Table 2. These data showed that the q_{max} values obtained by using biofilm, activated carbon and *E. coli* ASU 7 were 97.70, 90.70, and
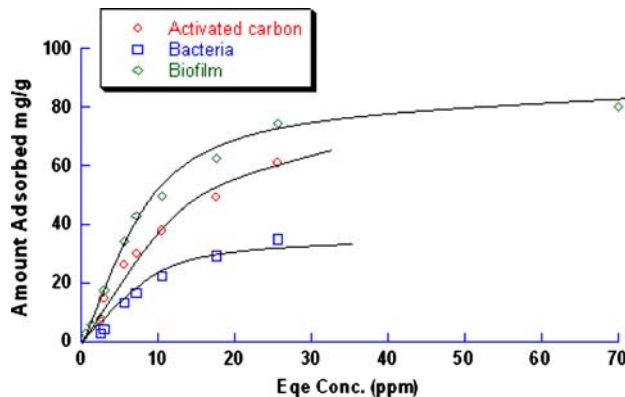
64.36 mg metal/g biomass for Cr^{6+}, respectively. However, the b values for biofilm, GAC and *E. coli* ASU 7 were 0.099, 0.035, and 0.053, respectively. These values indicated that biofilm possesses have a high adsorption affinity for Cr^{6+}. Furthermore, these results indicate that the biofilm as biosorbent is more efficient than other biosorbents because the biofilm formed on the GAC can change the surface charge density of the GAC.

Freundlich adsorption isotherms

Another model which usually used for analyzing the adsorption data is the Freundlich equation and its linear form (Volesky and Holan 1995). Linear transformation of the data using the Freundlich model as in Fig. 7 and the values of Freundlich parameters are summarized in Table 2. These data show that the adsorption capacity K_f for Cr^{6+} using biofilm, GAC and bacteria were 1.39, 1.17, and 1.11, respectively. Here it is worth mentioning that the correlation
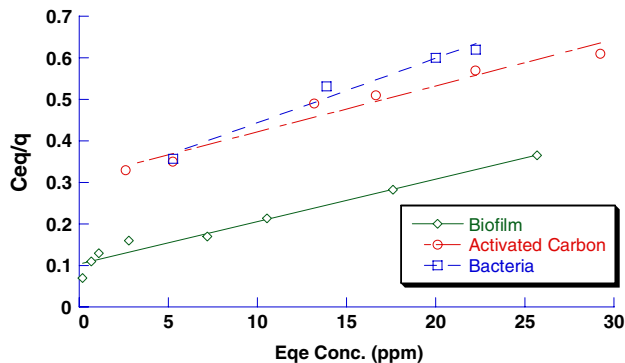

Fig. 6 The linearized Langmuir adsorption isotherm of hexavalent chromium by biofilm ($\diamond$) activated carbon (o) and *E. coli* ASU 7 ($\square$) at 30°C, pH 2 and equilibrium time at 30 min

Table 2 Gives a comparative data obtained from the adsorption of hexavalent chromium ion on the surface of biofilm, activated carbon and bacteria upon the application of the two different models given by Langmuir and Freundlish adsorption isotherm equations

Biosorbent	Langmuir			Freundlish		
	q_{max} (mg/g)	b (l/mg)	r^2	K_f	n	r^2
Biofilm	97.7	0.099	0.98	1.39	3.39	0.92
Activated carbon	90.7	0.035	0.98	1.17	5.26	0.96
Bacteria	64.36	0.053	0.98	1.11	3.89	0.98

Langmuir and Freundlish parameters are calculated according to Volesky and Holan (1995)
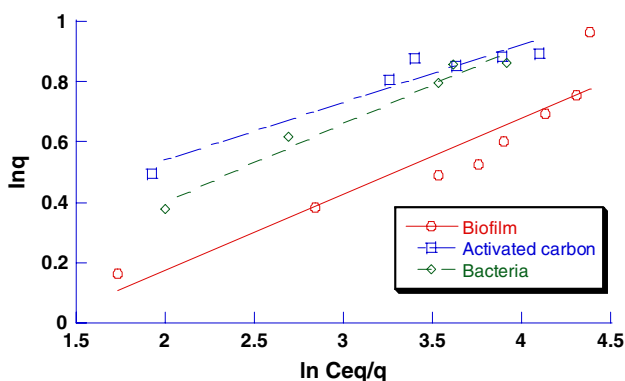

Fig. 7 The linearized form of Freundlish adsorption isotherm of Cr^{6+} of *E. coli* ASU 7 ($\square$), activated carbon (o) and biofilm ($\diamond$) at 30°C, pH 2 and equilibrium time at 30 min

coefficients for all the biosorption measurements of Cr^{6+} using different biosorbents were found to be close to unity (0.92).

In general, these data indicate that the sorption capacity increased with increasing the initial metal ion concentrations correspond to metal ion on the biomass surface. This sorption characteristic indicates that the surface saturation is dependent on the initial metal ion concentrations. At low concentrations, adsorption sites took up the available metal more quickly. However, at higher concentrations metals need more time to diffuse into the biomass surface by intraparticular diffusion and greatly hydrolyzed ions will diffuse at a slower rate. From the above findings, one can conclude that the biofilm is a potent biosorbent for giving a value of Cr^{6+} 97.70 mg/g dry wt.

Conclusions

From the laboratory-based experiments, the following conclusions can be reached: the optimum pH for hexavalent chromium biosorption is 2.0, after 30 min at room temperature. The biosorption equilibrium data fitted well to both Langmuir and Freundlich model for Cr^{6+} as metal ion in the studied concentration range.

The mechanism of biosorption includes mainly ionic interactions and formation of complexes between metal and acidic sites in the cell wall of bacterium and this was confirmed by IR and pH experiments. The maximum adsorption uptake (q_{max}) of hexavalent chromium calculated from Langmuir equation for biosorption by biofilm, GAC and bacteria are 97.7, 90.7, 64.36 mg/g, respectively.

The results demonstrate that biofilm supported on GAC, which prepared by impregnation method could be used as promising biosorbent for the removal of Cr^{6+} ions from aqueous solutions.

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